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INTERMOLECULAR POTENTIAL AND PROPERTIES OF ARGON

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ABSTRACT. By utilising the recent compressibility data, the potential field of argon has been determined on the Lennard-Jones (12:6) and (9:6) models. The force constants thus determined on the L-J (12:6) model give a better correlation of the various properties of argon than those obtained previously. A consideration of the equilibrium properties of argon lends support to the suggestion of Kihara that the potential bowl of the spherical molecules should be wider than that given by the L-J (12:6) model.

INTRODUCTION

Considerable progress has already been made in correlating the various bulk properties of molecules and particular success has been achieved in the case of spherical molecules. One of the most common forms of the intermolecular potential used for this purpose is the Lennard-Jones $(n : m)$ potential

$$\phi(r) = \epsilon \left[\frac{m}{n-m} \left(\frac{r_m}{r} \right)^n - \frac{n}{n-m} \left(\frac{r_m}{r} \right)^m \right] \qquad \ldots \ (1)$$

where r is the distance between the two molecules and $-\epsilon$ is the potential minimum at $r = r_m$. The quantity r_m is related to σ_n, the value for which $\phi(r) = 0$, by the relation

$$\sigma_n = r_m \left(\frac{m}{n} \right)^{\frac{1}{n-m}} \qquad \ldots \ (2)$$

Theoretical considerations lead us to assume $m = 6$, but it is impossible to fix n from theory and it is usual to determine n from best empirical fit.

Even for spherical molecules, there remains some uncertainty about the best value of the index n. Several workers, Hirschfelder, et al. (1948), Srivastava and Madan (1953a, 1953b) and others have shown that the transport properties can be represented reasonably well with $n = 12$. Unfortunately due to difficulty in evaluating the complicated collision integrals for the transport properties, these have till now been evaluated only for $m = 6$, $n = 12$ (Hirschfelder, et. al., 1954) and for $m = 4$, $n = 8$ (Clark-Jones, 1940).

It has been found that amongst the equilibrium properties the second virial coefficient $B(T)$ is rather insensitive to the form of potential chosen. The reason

for this may be found in the recent work of Kellar and Zumino (1959) which shows that $B(T)$ alone can determine only the repulsive part and the width of the inter-molecular potential as a function of its depth. So it appears that from a considera-tion of $B(T)$ data at sufficiently high temperatures (where the repulsive part of the potential is more important), it should be possible to find the best value of n. Unfortunately, no such data exist. A serious disadvantage in using the third virial coefficient, $C(T)$ (which is sensitive to the potential form chosen), for deter-mining the intermolecular potential is the difficulty of obtaining accurate values of $C(T)$, unless the compressibility data are very accurate. However, Bahadur and Madan (1960) have tried to obtain the force parameters on the $L-J$ (12 : 6) potential from $C(T)$ data by drawing smooth curves. Very recently, Guggenheim and McGlashan (1960) have obtained a five parameter potential for argon by utilising mainly the various crystal properties. It has however been shown by Jansen and McGinnies (1956) that in the crystalline state the assumption of pair-wise additivity of the molecular forces is not strictly valid. The three-body long range forces in a crystal have been found to contribute a sizeable portion of the total Van der Waals interaction energy which becomes greater, the heavier the atom and the higher the density of the crystalline medium. Consequently, the treatment of Guggenheim *et. al.*, which is based on two-body forces, is some-what uncertain.

Kihara (1953, 1955), from a consideration of $B(T)$ and $C(T)$ values suggested that at least for the spherical molecules, the potential bowl should be wider than that given by $L-J$ (12 : 6) potential, and $L-J$ (9 : 6) model might give better representation of the various molecular properties. However, some of the $C(T)$ values used by Kihara were not very reliable. Other workers Hirschfelder, *et al.*, (1954), Beattie (1952) and Michels (1958), have also found that the $L-J$ (12 : 6) potential is incapable of giving a completely satisfactory representation of the various equilibrium properties and have suggested that the discrepancies may be due to incorrectness of the potential form. It appears therefore that Kihara's suggestion requires further investigation. For this purpose we have chosen to consider the case of argon for which compressibility and other experi-mental data exist in the literature in the hope that a thorough consideration of various properties of argon may clear up some of the uncertainties. Attempts have also been made to get a set of force constants on the $L-J$ (12 : 6) model which will give a better correlation of the various properties of argon than that obtained hitherto.

DETERMINATION OF THE PARAMETERS

We have followed the procedure of Whalley and Schneider (1955) in fitting the experimental second virial data to the Lennard-Jones (12 : 6) and (9 : 6) poten-tials. The data used are those recently published by Michels *et al.* (1958) together

with their earlier determinations (1949) in the temperature range from $-150°C$ to $+150°C$. The second virial coefficient $B(T)$ may be written as

$$B(T) = \rho B^*(T^*) \qquad \qquad \ldots \text{ (3)}$$

where ρ is a constant depending on σ and $B^*(T^*) = B(T)/B(T)_{rig \cdot sph}$. The tables of B^* as a function of T^* have been obtained for the L—$J(12:6)$ model by Hirschfelder, *et al.* (1954) and for L—J $(9:6)$ model by Epstein and Hibbert (1952). First the parameter ρ (which gives σ) and ϵ/k have been obtained approximately by following the graphical procedure of Lennard-Jones (1924). In order to determine ρ and ϵ/k more accurately the method of least squares (Deming 1943) has been applied as follows :

Let the approximate values of ρ and ϵ/k determined graphically be ρ_0 and $(\epsilon/k)_0$ and

$$\epsilon/k = (\epsilon/k)_0 - K \qquad \qquad \ldots \text{ (4)}$$

$$\rho = \rho_0 - L \qquad \qquad \ldots \text{ (5)}$$

where K and L are small correction terms. Then the normal equations for computing the correction terms are written as

$$\Sigma(KF_{\epsilon/k} + LF_\rho + F_0)F_\rho = 0 \qquad \qquad \ldots \text{ (6)}$$

$$\Sigma(KF_{\epsilon/k} + LF_\rho + F_0)F_{\epsilon/k} = 0 \qquad \qquad \ldots \text{ (7)}$$

with

$$F_0 = B(T) - \rho B^*(T^*)$$

$$F_{\epsilon/k} = -[\rho/(\epsilon/k)] \cdot T^* \left(\frac{dB^*}{dT^*} \right)$$

$$F_\rho = B^*(T^*).$$

TABLE I

Parameters on L—J $(12:6)$ and $(9:6)$ potentials

Authors	L-J (12:6) model		L-J (9:6) model	
	σÅ	$\epsilon/K°K$	σÅ	$\epsilon/K°K$
Present work	3.418	120.23	3.584	89.59
Michels, et al. (1949)	3.405	119.8	—	—
Whalley and Schneider (1955)	3.409	119.49	3.567	89.64
Hirschfelder, et al. from viscosity (1954)	3.418	124	—	—
Bahadur and Madan (1960)	3.419	120.5	—	—

Here F_0, $F_{\epsilon/k}$ and F_ρ are to be calculated using the absolute values $(\epsilon/k)_0$ and ρ_0. Eqs. (6) and (7) are then solved for K and L. If the difference between $(\epsilon/k)_0$ and ρ_0, and ϵ/k and ρ comes out to be more than a few percent the fitting is done by using better approximations.

The force constants thus determined on $L-J$ (12 : 6) and (9 : 6) models are shown in Table I, together with the values obtained by other workers.

COMPARISON WITH EXPERIMENT

(a) Equilibrium Properties

(i) Second Virial and Third Virial Coefficients

The experimental and calculated values of second virial coefficient $B(T)$ and the third virial coefficient $C(T)$ on Lennard-Jones (12 : 6) and (9 : 6) models are shown in Table II. For $B(T)$ it is not possible to determine the superiority of the $L-J$ (12 : 6) or the $L-J$ (9 : 6) potential over the other. It is, however, to be noted that Michels, *et al.* (1958) could not fit their $B(T)$ data at lower temperatures on the $L-J$ (12 : 6) models with the force constants previously determined by them (1949). It will be seen that with the force constants deter-

TABLE II

Experimental and calculated values of $B(T)$ and $C(T)$ on the $L-J$ (12 : 6) and $L-J$(9 : 6) models

T °K	B(T) (c.c./mole)				C(T) (c.c./mole)²		
	Expt.	L-J (12:6) calc.	L-J (12:6) from Michels et al.	L-J (9:6) calc.	Expt.	L-J (12:6) calc.	L-J (9:6) model
133.2	−107.98	−106.79	−104.95	−104.79	2656	1426	1976
138.2	−100.88	− 99.69	− 98.13	− 98.04	2418	1478	1964
143.2	− 94.43	− 92.86	− 92.22	− 92.19	2417	1503	1943
148.2	− 88.45	− 87.95	− 87.36	− 86.77	2357	1505	1913
150.7	− 85.64	− 85.34	− 83.68	− 84.20	2313	1504	1899
153.2	− 82.97	− 82.81	− 81.26	− 81.79	2278	1499	1882
163.2	− 73.25	− 73.31	− 72.23	− 72.77	2104	1468	1810
173.2	− 65.21	− 65.63	− 63.68	− 65.05	2015	1416	1740
188.2	− 54.83	− 55.40	− 54.16	− 55.11	1791	1336	1637
203.2	− 46.83	− 47.14	− 45.95	− 46.93	1711	1255	1571
223.2	− 37.43	− 38.36	− 37.27	− 37.91	1541	1175	1451
248.2	− 28.57	− 30.61	− 28.46	− 28.96	1365	1085	1340
273.2	− 21.45	− 21.95	− 21.49	− 21.92	1270	1020	1279
298.2	− 15.75	− 15.83	− 15.93	− 15.98	1160	977	1241
323.2	− 11.24	− 11.65	− 11.16	− 11.38	1130	935	1176
348.2	− 7.25	− 7.48	− 7.28	− 7.36	1040	905	1139
373.2	− 4.0	− 4.10	− 3.98	− 3.94	1000	883	1110
398.2	− 1.18	− 1.34	− 1.14	− 1.046	970	866	1084
423.2	+ 1.38	+ 1.23	+ 1.31	+ 1.34	880	852	1062

mined in this paper, the low temperature $B(T)$ values of argon can also be represented satisfactorily on the $L-J(12:6)$ model.

The agreement between the experimental and the calculated values of $C(T)$ is not good either for the $L-J$ $(12:6)$ or $L-J$ $(9:6)$ potential, but is definitely better on $L-J$ $(9:6)$ model.

(ii) *Joule-Thomson coefficient*

The Joule-Thomson Coefficient at zero pressure μ^0 may be written on the $L-J$ $(12:6)$ model as

$$\mu^0 C_p^0 = b_0(B^*_1 - B^*) \qquad \qquad \ldots \quad (8)$$

TABLE III

Experimental and the calculated values of the J $-$T coefficient of argon at zero pressure in °C atm^{-1}

T °K	$\mu^0 \times 10^3$ Expt. (a)	$\mu^0 \times 10^3$ on the L-J (12:6) model	$\mu^0 \times 10^3$ on the L-J (9:6) model
123.2	1.750	1.648	1.527
137.7	1.293	1.386	1.311
148.2	1.075	1.217	1.155
160.7	0.935	1.070	1.026
173.2	0.835	0.988	0.9022
185.7	0.756	0.884	0.8034
198.2	0.695	0.736	0.7211
223.2	0.578	0.632	0.587
248.2	0.4905	0.522	0.492
273.2	0.418	0.445	0.419
298.2	0.360	0.388	0.362
323.2	0.312	0.330	0.314
348.2	0.270	0.304	0.2745
373.2	0.236	0.245	0.239
398.2	0.204	0.214	0.207
423.2	0.178	0.186	0.181
473.2	0.134	0.140	0.129

(a) J. R. Roebuck and H. Osterberg, (1934)

where $C_p{}^0$ is the zero pressure value of the molar specific heat, $b_0 = \frac{2}{3}\pi N \sigma^3$ and $B_1{}^* = T^* \cdot \dfrac{dB^*}{dT^*}$. The $B^*{}_1$ and B^* have been tabulated as a function of T^* (Hirschfelder *et al.*, 1954).

On the $L-J$ (9 : 6) model Epstein and Hibbert (1952) have calculated the values of B^* as a function of $1/T^*$. From these tables the values of B^* and $B^*{}_1$ as functions of T^*, required for calculating $\mu^0 C_p{}^0$ were obtained graphically. The values thus obtained are given in appendix which may be utilized for the calculation of μ^0 on the $L-J$ (9 : 6) model. The experimental and the calculated values of μ^0 on different molecular models are given in Table III. It is interesting to note that Hirschfelder (1938) could not fit the experimental μ^0 data for argon on the $L-J$ (12 : 6) model. Table III shows that the $L-J$ (9 : 6) potential gives a better agreement with the experimental values of μ^0 than the $L-J$ (12 : 6) model.

(iii) *Crystal properties*

The heat of sublimation, $\Delta H_s(0)$ and the lattice spacing, R, both at $0°K$ are simply correlated with the inter-molecular potential provided the substance crystallizes in the cubic system. The equations for the lattice spacing including the effect of zero point energy have been given by Corner (1948) for $(n : 6)$ potential which have been reduced for the $L-J$ (12 : 6) and $L-J$ (9 : 6) potential as follows :

For the $L-J$ (12 : 6) potential,

$$C_6 = 2C_{12}\left(\frac{\sigma}{R}\right)^6 + \left\{\frac{h^2}{8\pi^2 m_c \sigma^2}\right\}^{\frac{1}{2}} \cdot \frac{77C_{14}\left(\dfrac{\sigma}{R}\right)^6 - 10C_8}{\left\{22C_{12}\left(\dfrac{\sigma}{R}\right)^{10} - 5C_8\left(\dfrac{\sigma}{R}\right)^4\right\}^{\frac{1}{2}}} \qquad \ldots \quad (9a)$$

and for $L-J$ (9 : 6) potential

$$C_6 = C_9\left(\frac{r_m}{R}\right)^3 + \left\{\frac{h^2}{3\pi^2 m_c r^2{}_m}\right\}^{\frac{1}{2}} \cdot \frac{11C_{11}\left(\dfrac{r_m}{R}\right)^3 - 5C_8}{4C_{11}\left(\dfrac{r_m}{R}\right)^7 - \dfrac{5}{2}C_8\left(\dfrac{r_m}{R}\right)^4} \qquad \ldots \quad (9b)$$

where $r_m =$ value of r at potential minimum

$h =$ Planck's constant

$m =$ mass of the molecule

and C_n for $n = 1, 2$, etc. are numerical constants calculated by Lennard-Jones and Ingham (1925). Using the force constants determined in the present paper, the value of R was evaluated from Eqn. (9). This value of R was used for calculating the $\Delta H_v^{(0)}$ with the help of equation given below for $(n : 6)$ potential.

$$\Delta H_v^{(0)} = \frac{1}{2} N\epsilon \left[6C_n \left(\frac{r_m}{R} \right)^n - nC_6' \left(\frac{r_m}{R} \right)^6 \right] (n-6) \qquad \ldots \quad (10)$$

The values of $\Delta H_v^{(0)}$ and R thus obtained together with the experimental values are given in Table IV. It is to be noted that the crystal data cannot give any definite information about the suitability of any particular form of potential as it has been shown by McGinnes and Jansen (1956) that the assumption of the additivity of molecular force is not possibly valid in the crystalline state. Consequently, equations (9) and (10) which are based on this assumptions are somewhat uncertain.

TABLE IV

Experimental and calculated values of $\Delta H_v^{(0)}$ and R for argon

Authors	$H_v^{(0)}$ in cal./mole			R in Å		
	Expt.	Calculated		Expt.	Calculated	
		L-J (12:6)	L-J (9:6)		L-J (12:6)	L-J(9:6)
Present work	a 1998±40	2010	1722	b 3.81	3.73	3.908
Whalley and Schneider		2033±6	1718±5		3.767	3.929

(a) Whalley and Schneider, (1955)

(b) Simon and Von Simon, (1924)

(b) Transport properties

(i) Viscosity

The experimental and the calculated values of viscosity of argon on L-J (12 : 6) model have been given in Table V. The agreement of calculated values with the experimental data is better than that obtained by using Michels' force constants. It has long been known that the high temperature viscosity data of argon cannot be represented well by the L-J (12 : 6) potential. This may be due to the increasing importance of the repulsive part of the intermolecular potential at high temperature which should vary exponentially rather than obey an inverse power law.

(ii) Thermal conductivity

The experimental and calculated values of the thermal conductivity of argon is given in Table VI. The theoretical values were calculated to the first approxi-

TABLE V

Experimental and calculated values of viscosity of argon (in 10^{-7} gm/cm.sec)

T °K	Expt.	Calculated from our constants	Calculated from force constants of Michels, (*et al*).	Calculated from force constants from viscosity	Ref for Expt. data
80	688	660	666	649	a
120	993	997	1005	979	a
160	1298	1319	1332	1300	a
200	1594	1620	1636	1601	a
240	1878	1902	1920	1882	a
280	2145	2166	2182	2143	a
298	2228	2274	2279	2267	b
575	3685	3704	3737	3682	c
676	4115	4133	4169	4111	c
800	4621	4662	4698	4641	a
1200	5947	6066	6113	6083	a
1500	6778	6953	7161	6983	a

(a) Johnston and Grilly, (1942) (b) Kestin and Leidenpost (1959)
(c) Trautz Melster and Zink, (1930)

mation on the Chapman-Enskog theory (Hirschfelder, *et al.*, 1954). It may be seen that the force constants determined in the present work from the second virial coefficient can represent the thermal conductivity of argon almost as satisfactorily as those determined from viscosity.

TABLE VI

Experimental and calculated values of the thermal conductivity K (in 10^{-7} cal. cm^{-1}. sec^{-1}. deg^{-1}.) for argon.

T °K	Expt (a)	Calculated from our force constants	Calculated from force constants of Michel, *et al.*	Calculated from force constants from viscosity
90.23	141	139	140	137
194.7	293	295	298	292
273.2	394	395	399	392
373.2	506	505	509	504
491.2	614	618	623	619
579.2	684	694	700	696

(a) Kannuluik and Carman, (1952)

CONCLUSIONS

(1) A consideration of the equilibrium properties of argon lends support to the suggestion of Kihara that the potential bowl of the spherical molecules should be wider than that given by the $L-J$ (12 : 6) model. The fact that the high temperature transport properties require a value of index of repulsion higher than 12 may be due to the inadequacy of inverse power repulsion at higher temperature. Hence at moderate temperature a $L-J$ (9 : 6) model may possibly give a better representation of the potential field, than a $L-J$ (12 : 6) potential.

(2) The set of force constants obtained on the $L-J$ (12 : 6) potential in this paper gives a more consistent representation of the various properties of argon than those hitherto obtained.

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APPENDIX

The values of B^* and $T^* \dfrac{dB^*}{dT^*}$ on the $L-J$ (9 : 6) model were obtained graphically from the table given by Epstein and Hibbert (1952). The values thus obtained are given in Table VII. This table may be used to calculate the Joule-Thomson Coefficient at zero pressure on the $L-J$ (9 : 6) model.

TABLE VII

Table for B^* and $B_1^* = \dfrac{dB^*}{dT^*}$. T^* for calculating μ^0, the zero-pressure Joule-Thomson Coefficient on $L—J$ $(9:6)$ model

T^*	B^*	B_1^*	T^*	B^*	B_1^*
0.5	−11.19	17.25	3.1	−0.355	1.085
0.55	− 9.40	16.51	3.2	−0.322	1.043
0.60	− 7.94	13.80	3.3	−0.275	1.010
0.65	− 6.98	11.70	3.4	0.248	0.975
0.70	− 6.17	10.15	3.5	−0.220	0.940
0.75	− 5.52	9.00	3.6	−0.188	0.923
0.85	− 4.52	7.31	3.7	−0.163	0.882
0.90	− 4.04	6.58	3.8	−0.134	0.857
0.95	− 3.74	6.03	3.9	−0.110	0.835
1.0	− 3.46	5.3	4.0	−0.085	0.810
1.1	− 2.97	4.62	4.1	−0.068	0.788
1.2	− 2.56	4.03	4.2	−0.052	0.765
1.3	− 2.25	3.62	4.3	−0.033	0.740
1.4	− 2.00	3.23	4.4	−0.017	0.72
1.5	− 1.78	2.91	4.5	−0.002	0.695
1.6	− 1.58	2.69	4.6	+0.012	0.680
1.7	− 1.42	2.49	4.7	+0.028	0.665
1.8	− 1.29	2.29	4.8	+0.042	0.650
1.9	− 1.15	2.12	4.9	+0.053	0.638
2.0	− 1.05	1.96	5.0	+0.063	0.620
2.1	− 0.958	1.84	6.0	+0.161	0.568
2.2	− 0.868	1.702	7.0	+0.23	0.426
2.3	− 0.787	1.602	8.0	+0.28	0.356
2.4	− 0.714	1.502	9.0	+0.317	0.302
2.5	− 0.646	1.410	10.0	+0.346	0.245
2.6	− 0.585	1.338	11.0	+0.365	0.187
2.7	− 0.530	1.27	12.0	+0.381	0.150
2.8	− 0.477	1.21	13.0	+0.395	0.104
2.9	− 0.435	1.165	14.0	+0.405	0.084
3.0	− 0.390	1.11	15.0	+0.416	0.0675

A NOTE ON SOME TUNABLE OSCILLATORS

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ABSTRACT. Some arrangements of voltage tunable two-path oscillators capable of large frequency deviation are discussed. Possible combinations of the transfer functions of the individual paths together with the tuning equation and the constraints for stable amplitude of oscillation are given. In some circuit arrangements the variation of frequency with modulating voltage is found to be linear over a wide range.

The present note discusses some circuit arrangements of voltage tunable oscillators which are theoretically capable of very large frequency deviation. In practical arrangements a frequency tuning ratio of two to one and in some cases five to one have been achieved. Tuning is accomplished by means of variation of the gains of the individual paths of a two-path oscillator.
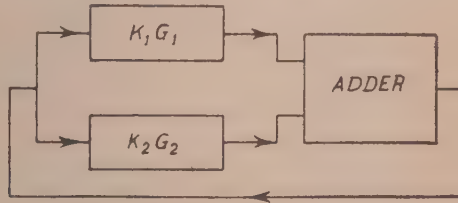
Fig. 1. Schematic diagram of a two-feedback loop.

If $G_1(p)$ and $G_2(p)$ are the transfer functions of the two paths of the feedback loop in Fig. 1 the characteristic equation of the loop is given by

$$K_1 G_1 + K_2 G_2 = 1 \qquad \dots \quad (1)$$

Here K_1 and K_2 are the gain multiplying factors and are in general variable in accordance with the tuning voltage. If the adder is non-ideal and has a transfer function $F(p)$ then Eq. (1) is modified to

$$K_1 G_1 + K_2 G_2 = \frac{1}{F} \qquad \dots \quad (1.a)$$

The condition for proper working is that the imaginary axis be the root locus with unity feedback.

In Table I some possible combinations of transfer functions together with the tuning equation and the constraints for stable amplitude of oscillation are

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presented. All the circuits have the property that in theory it should be possible to tune their frequency of operation electronically from very low to very high frequencies. Furthermore the magnitude of their positive feedback voltage should be independent of the frequency of resonance. In some arrangements the curve of frequency versus modulating voltage is linear over a wide range. In a few arrangements where the stray capacitances can be taken into account in forming the transfer functions the tuning range can obviously be extended to figure of merit of the tubes employed or a fraction of it depending on the gain required.

It will be observed that types 1-6 are practical at audio frequencies, types 1, 5 and 6 at low and very low frequencies, while types 1, 6, 7 and 8 are useful at radio frequencies. In Fig. 2(a) and Fig. 2(b) are presented circuit arrangements
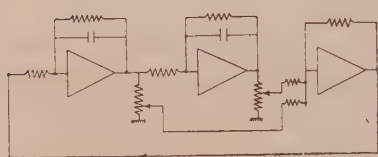
Fig. 2(a). Schematic diagram of the circuit arrangement of type 1 for low and very low frequencies
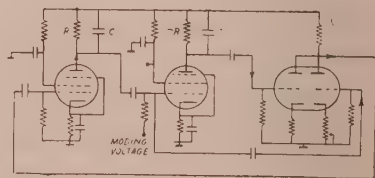
Fig. 2(b). Schematic diagram of the circuit arrangement of type 1 for A. F. and R. F.

of oscillator of type 1 for use at low and at radio frequencies. For RF an interesting form derived from type 6 making use of delay lines can be made as shown in Fig. 3(a) and (b). Its tuning equation is

$$w\delta = \cos^{-1}(-K_1/2) \qquad \qquad \cdots \quad (2)$$
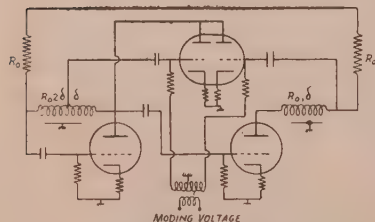
Fig. 3(a). Schematic diagram of a circuit arrangement of type 6.
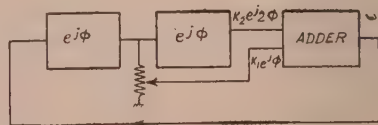
Fig. 3(b). Functional diagram of type 6.

The frequency of excursion in this case is limited to $\dfrac{1}{2\delta}$. The linearity of modulation around $\dfrac{1}{4\delta}$ has been observed to be quite good. It is to be noted that

TABLE I

Type	$G_1(j\omega)$	$G_2(j\omega)$	Constraint	Tuning equation	Differential equation	Working frequency
1	$\dfrac{1}{1+j\omega}$	$-\dfrac{1}{(1+j\omega)^2}$	$K_1 = 2$	$\omega = \sqrt{K_2 - 1}$	$\dfrac{d^2 x}{dt^2} + 2\dfrac{dx}{dt} + x + K_2 x - \dfrac{d}{dt} F(x) - F(x) = 0$	L.F., A.F. & R.F.
2	$\dfrac{\omega}{1+j\omega}$	$-\left(\dfrac{j\omega}{1+j\omega}\right)^2$	$K_1 = 2$	$\omega = \dfrac{1}{\sqrt{K_2 - 1}}$	$\dfrac{d^2 x}{dt^2}(1+K_2) + 2\dfrac{dx}{dt} + x - \dfrac{d^2}{dt^2}F(x) - \dfrac{d}{td}F(x) - 3$	A.F.
3	$\dfrac{1}{1+j\omega}$	$\dfrac{j\omega}{(1+j\omega)^2}$	$K_1 + K_2 = 2$	$\omega = \sqrt{K_2 - 1}$	$\dfrac{d^2 x}{dt^2} + 2\dfrac{dx}{dt} + x - F(x) - \dfrac{d}{dt}F(x) - K_2\dfrac{dx}{dt} = 0$	A.F.
4	$\dfrac{1}{1+j\omega}$	$\dfrac{1-j\omega}{(1+j\omega)^2}$	$K_1 - K_2 = 2$	$\omega = \sqrt{2K_2 - 1}$	$\dfrac{d^2 x}{dt^2} + 2\dfrac{dx}{dt} + x - K_2 x + K_2\dfrac{dx}{dt} - F(x) - \dfrac{d}{dt} = 0$	L.F., A.F. & low F.R.
5	$\dfrac{1-j\omega}{1+j\omega}$	$\left(\dfrac{1-j\omega}{1+j\omega}\right)^2$	$K_2 = -1$	$\omega = \sqrt{\dfrac{2-K_1}{2+K_1}}$	$\dfrac{d^2 x}{dt^2} + 2\dfrac{dx}{dt} + x - K_1 x + K_2\dfrac{d^2 x}{dt^2} + \dfrac{d^2}{dt^2}F(x) + 2\dfrac{d}{dt}F(x) - F(x) = 0$	L.F., A.F. & low R.F.
6	$e^{jF(\omega)}$	$e^{j2F(\omega)}$	$K_2 = -1$	$F(\omega) = \cos^{-1}\dfrac{K_1}{2}$	$x(t) - K_1 x(t-\delta) + F(x(t-2\delta)) = 0$ if $F(\omega) = -\omega\delta$.	R.F.
7	$\dfrac{1-e^{-j\omega\delta}}{1+e^{-j\omega\delta}}$	$-\left(\dfrac{1-e^{-j\omega\delta}}{1+e^{-j\omega\delta}}\right)^2$	$K_1 = 0$	$\omega = \dfrac{2}{\delta}\tan^{-1}\sqrt{\dfrac{1}{K_2}}$	$x(t) + 2x(t-\delta) + x(t-2\delta) + F(x(t)) - 2F(x(t-\delta)) + F(x(t-2\delta)) = 0$	R.F.
8	$\dfrac{1+e^{-j\omega\delta}}{1-e^{-j\omega\delta}}$	$-\left(\dfrac{1+e^{-j\omega\delta}}{1-e^{-j\omega\delta}}\right)^2$	$K_1 = 0$	$\omega = \dfrac{2}{\delta}\cos^{-1}\sqrt{\dfrac{1}{K_2}}$	$x(t) - 2x(t-\delta) + x(t-2\delta) + F(x(t)) - 2F(x(t-\delta)) + F(x(t-2\delta)) = 0$	R.F.

in arrangements of types 6, 7 and 8, means will have to be adapted to supress harmonics.

The forms 1—5 have identical characteristic equations. However the way nonlinearities enter into the equation is different and consequently the amplitude stability and other related properties will be different. The nonlinear defining equations in the different cases are also presented in Table I. $F(x)$ represents the nonlinear parameter basically governing the amplitude of oscillation.

It has been found that the variation of frequency is limited in practice to a ratio of five to one in types 1—5, while in the rest it is about two to one. It is thought that this may be due to the very considerable variation of the slope of the loop phase shift. Another cause is the non-ideal behaviour of the adder.

The disturbing effect of the adder can be removed in the following manner. Supposing that the transfer function of the adder $\dfrac{b}{p+b}$, is the modified loop, equation is

$$(K_1G_1+K_2G_2) \cdot \frac{b}{p+b} = 1 \qquad \qquad \dots \quad (1.c)$$

The characteristic equation of the loop in the oscillating condition will now be

$$(p^2+K)(p+C) = 0 \qquad \qquad \dots \quad (3)$$

It will be found in this case that both K_1 and K_2 are to be varied. For type 1 for example K_1 and K_2 are related by

$$(2b+1)(2+b) = K_1b(2+b)+b(1-K_1-K_2) \qquad \dots \quad (4)$$

TUNABLE AMPLIFIERS

It is evident that at a gain setting smaller than that required for self-oscillation all the circuits can be used as tunable amplifiers and hence as spectrum analysers. The nature of the selectivity curve and the variation of the maximum output of the response curve with the tuning frequency will obviously depend on the point of observation of the output as well as the nature of the transfer functions. In the diagram of Fig. 1 for example for inputs E_1, E_2 and E_A applied respectively at the input to G_1 circuit, G_2 circuit and the adder the voltage outputs at the corresponding output points will be given by

$$\frac{e_1}{G_1} = f \cdot (K_1G_1E_1+K_2G_2E_2+E_A)+E_1, \qquad \dots \quad (5.a)$$

$$\frac{e_2}{G_2} = f \cdot (K_1G_1E_1+K_2G_2E_2+E_A)+E_2, \qquad \dots \quad (5.b)$$

$$e_A = f \cdot (K_1G_1E_1+K_2G_2E_2+E_A) \qquad \dots \quad (5c)$$

where

$$f = \frac{1}{1 - K_1 G_1 - K_2 G_2^-} \cdot$$

In the arrangement of Fig. 1, for example. if E_A be the input applied to the adder the output e_2 will be given by

$$e_2 = \frac{G_2}{1 - K_1 G_1 - K_2 G_2} E_A = \frac{1}{(2 - K_1) j w_0} E_A, \qquad \text{at } p = j w_0.$$

The peak of response will therefore depend on the tuning frequency. If on the other hand, the voltage obtained at the output of G_1 circuit is transmitted through a circuit having a transfer function $\frac{p}{p+1}$ one obtains a transfer character-istic which does not depend on the tuning frequency. It should be noted that a much simpler solution is possible for the arrangement of type 3.

<div align="center">REFERENCES</div>

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RAMAN, INFRARED AND LUMINESCENCE SPECTRA OF SOME TRISUBSTITUTED BENZENES

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Plate VIII

ABSTRACT. In the present paper tentative assignment of the vibrational frequencies of the molecules of 2, 4-and 3, 4-dichlorotoluene and 1, 2, 4-trichlorobenzene has been proposed from an analysis of the Raman and infrared spectra of the compounds. The Raman spectra of the dichlorotulenes have been investigated at −180°C and it has been observed that some of the intramolecular vibrations are affected and a few low frequency lines are exhibited by the compounds at the low temperature. Explanation of these changes has been offered in terms of association of the molecules at the low temperature. It has also been observed that in the solid state at −180°C both the compounds yield luminescence bands and the C=C valence oscillation appears to be coupled with the electronic transition giving rise to these bands.

INTRODUCTION

It is known from previous investigations (Biswas, 1954, 1955a,b; Sanyal, 1953) that the Raman spectra of mono- and disubstituted benzene compounds undergo changes and new low frequency Raman lines appear in the spectra with change of state and lowering of temperature, depending on the nature and relative positions of the substituents. In the present work, such investigation has been extended to two trisubstituted benzene compounds, viz., 2, 4- and 3, 4-dichloro-toluene. In order to understand the significance of the changes, it is necessary to assign the molecular frequencies, and both infrared and Raman spectra of the compounds were studied for this purpose. As a comparison with 1, 2, 4-trichloro-benzene would be helpful in making the assignments, the infrared spectrum of this compound was also recorded in the present investigation and the data for the Raman spectra obtained by Mukherjee (1960) have been utilised. The proposed assignments of the frequencies of all the three compounds and the observed changes in the Raman spectra of 2, 4- and 3, 4-dichlorotoluene with solidification have been discussed in this paper.

EXPERIMENTAL

The liquids were supplied by Fisher Scientific and Co., U.S.A. and were repeatedly subjected to both fractional and vacuum distillation before each exposure. In the case of the dichlorotoluenes two spectrograms, one with suit-

able light filters and another without filters, were obtained both for the liquid and solid states. The experimental arrangement for recording the Raman spectra in the solid state was the same as that reported earlier (Deb, 1960). The polarisation of the Raman lines was also studied by photographing the two components simultaneously with the help of a double image prism. The Raman spectra were photographed on Ilford Zenith plates using a Fuess glass spectrograph giving a dispersion of about 11 A per mm in the 4046 A region.

The infrared absorption spectra were recorded with a Perkin-Elmer Model 21 spectrophotometer with NaCl optics. Thin films of the liquids at the room temperature pressed between two rocksalt plates were used to obtain the absorption spectra.

RESULTS AND DISCUSSION

The spectrograms showing the Raman lines of 2. 4-and 3. 4-dichlorotoluene in the liquid and solid states are reproduced in Figs. 1 and 2. Plate VIII and the infrared absorption curves of the dichlorotoluenes and 1. 2, 4-trichlorobenzene are shown in Figs. 3. 4 and 5. The frequency shifts of the Raman lines and the observed infrared frequencies in cm^{-1} of the three compounds are given in Tables I, II and III. the Raman frequencies for 1. 2. 4-trichlorobenzene being taken from Mukherjee's results (Mukherjee. 1960). The state of polarisation of Raman lines are indicated by the letters 'P' and 'D' which mean 'polarised' and 'totally depolarised' respectively. The frequencies lower than 600 cm^{-1} could not be studied in the infrared because of the limitation of the NaCl optics used.

(a) *Assignment of molecular frequencies of 2, 4- and 3, 4- dichlorotoluene and 1, 2, 4- trichlorobenzene.*

The strong Raman lines at 705 cm^{-1}. 685 cm^{-1} and 675 cm^{-1} observed in the case of 2,4-dichlorotoluene. 3. 4-dichlorotoluene and 1. 2, 4-trichlorobenzene respectively (698. 682 and 675 cm^{-1} in the infrared) may be assigned to a C—Cl vibration arising from a_{1g}, b_{1u}, ϵ_{2g} and ϵ_{2u} vibrations in benzene, all of which become a'-type vibration in these compounds having C_s symmetry. The polarisation data support this assignment which is also in agreement with the results for mono- and dichlorobenzenes (Sponer and Kirby-Smith, 1941). There would also be components arising from these modes with frequencies of C—H valence oscillation of a'-type. They are likely to be represented by the lines 3062, 3062 and 3066 cm^{-1} for the three compounds. We should also expect a corresponding C—CH$_3$ stretching oscillation in the case of the dichlorotoluenes and actually the Raman spectra of the two dichlorotoluenes show lines at 1203 and 1211 cm^{-1} which should represent this vibration. there being no corresponding line in the spectrum of 1. 2, 4-trichlorobenzene. The depolarised lines 2926 cm^{-1} of 2. 4-dichlorotoluene and 2938 cm^{-1} of 3. 4-dichlorotoluene have also no counter-

3

TABLE I

Raman and infrared spectra of 2, 4-dichlorotoluene

Raman shift in cm⁻¹				Infrared bands
Liquid at 30°C			Solid at −180°C	Wave No, in cm⁻¹ and intensity
Landolt-Börnstein (1951)	Present authors			
			28 (3)	
			42 (1)	
			84 (4b)	
			101 (1)	
122 (3)	127 (2)	e, k D		
181 (7)	181 (6)	±e, k D	160 (1b)	
202 (8)	202 (8)	∓e, k D	205 (4b)	
265 (0)	269 (0)	k	268 (1)	
311 (5)	312 (6)	±e, k D	318 (3)	
378 (7)	380 (8)	±e, k P	380 (3)	
400 (3)	402 (3)	e, k P	401 (1)	
462 (4)	464 (4)	e, k P	464 (2)	
542 (0)				
645 (3)	646 (3)	e, k D	653 (1)	
704 (6)	705 (8)	e, k P	706 (6)	698 (w)
				799 (s)
832 (6)	834 (8)	e, k P	833 (6)	825 (s)
				852 (w)
				983 (w)
1046 (0)	1049 (1)	e, k	1048 (0)	1044 (ms)
				1088 (mb)
1105 (5)	1108 (4)	e, k P	1107 (2)	
				1122 (vw)
1143 (3)	1145 (4)	e, k P	1148 (0)	
1203 (5)	1204 (6)	e, k P	1210 (6)	
1251 (1)	1255 (1)	e, k P	1257 (0)	
	1302 (1)	e, k P	1301 (0)	
1378 (4)	1382 (6)	e, k P	1383 (5)	1372 (m)
1437 (0)	1438 (0)	e, k	1440 (0)	1438 (w)
				1460 (s)
				1558 (vw)
1590 (5b)	1592 (6b)	e, k D	1591 (1)	1580 (vw)
2929 (1)	2925 (4b)	e, k D	2926 (1)	
3061 (0)	3062 (1)	e, k	3060 (0)	

TABLE II

Raman and infrared spectra of 3, 4-dichlorotoluene

Raman shift in cm⁻¹		Infrared bands Wave No in cm⁻¹ and Intensity
Liquid at 30°C	Solid at −180°C	
	46 (1)	
	76 (1)	
127 (2b)±e, k D	145 (2)	
202 (6b)±e. D	202 (3)	
269 (0) e, k D	269 (0b)	
312 (6) ±e, k D	316 (1)	
368 (4) ±e, k P	366 (2)	
435 (6) ±e, k P	433 (4)	
463 (6) ±e, k P	461 (3)	
557 (obb) e, k		
624 (obb) e, k		
645 (ob) e, k	646 (0)	
686 (7) e, k P	680 (8)	682 (m)
		805 (vs)
870 (4) e, k P	870 (3)	865 (s)
		941 (vw)
		998 (vw)
1030 (4) e, k P	1026 (2)	1030 (s)
1101 (0) e	1100 (0)	
1135 (5) e, k P	1146 (2)	1130 (s)
	1170 (1)	1142 (vvw)
1211 (6) e, k P	1215 (6)	1211 (vvw)
		1258 (w)
1276 (1b) e, k D	1276 (0)	
1381 (4) e, k P	1377 (4)	1381 (s)
1443 (1b) e		1420 (vvw)
1457 (1b) e		
1470 (0) e		1469 (vs)
1598 (6) e, k D	1596 (1)	1592 (w)
2938 (5) e, k D	2938 (0)	
3062 (1) e, k P	3062 (0)	

TABLE III

Raman and infrared spectra of 1, 2, 4-trichlorobenzene

Raman shift in cm^{-1} Liquid at 30°C (Mukherjee, 1960)	Infrared bands Wave No. in cm^{-1} and Intensity
112 (2) e, k	
182 (2) e, k	
195 (4) e, k	
310 (1) e, k	
332 (3) ±e, k	
398 (2) e, k P	
459 (2) e, k	
673 (5) e, k	675 (m)
816 (0) e, k	810 (vs)
868 (0)*	865 (s)
1034 (3) e, k P	
	1052 (s)
1090 (1) e, k P	1096 (vs)
1124 (2) e, k	1122 (s)
1158 (4) e, k	
1261 (1)*	1243 (m)
1375 (0) e, k	1376 (s)
	1419 (w)
	1459 (vs)
	1490 (vw)
1571 (6b) e, k	1566 (s)
	1620 (vvw)
	1725 (vw)
3066 (5) k	3090 (m)

* These frquencies are taken from Landolt-Börnstein's (1951) tables.

part in the spectrum of 1, 2, 4-trichlorobenzene and are thus expected to arise from a mode of vibration in the methyl group. From analogy with other methylated, compounds, these have been attributed to the asymmetric stretching of the C—H bond in the methyl group.

Fig. 1

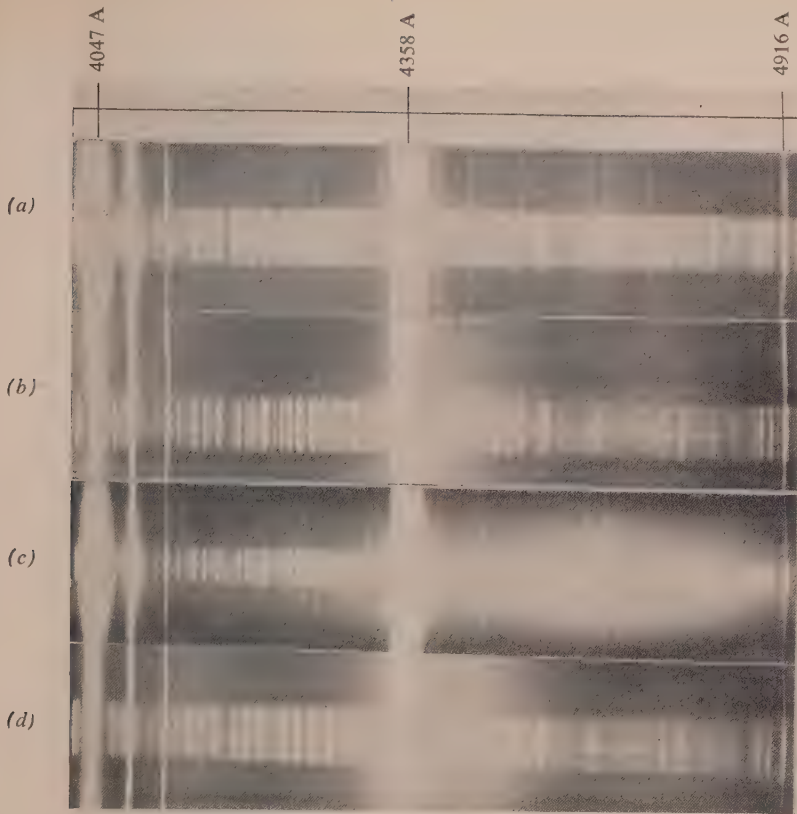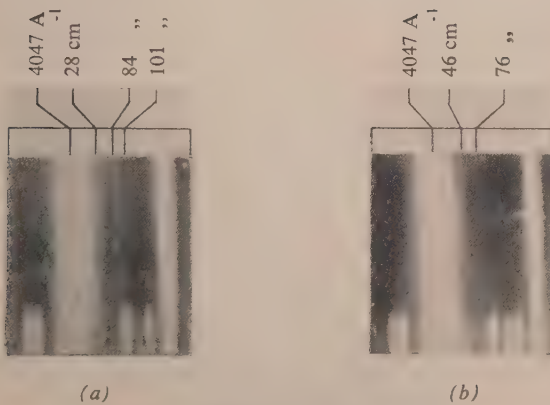(a)   (b)

Raman spectra

Fig. 1. (a) 2,4 - dichlorotoluene, liquid at 30°C
(b)   ,,   ,,   solid at −180°C
(c) 3,4 - dichlorotoluene, liquid at 30°C
(d)   ,,   ,,   solid at −180°C
Fig. 2. (a) Low-frequency Raman lines of 2,4 - dichlorotoluene at −180°C
(b) Low-frequency Raman lines of 2,4 - dibromotoluene at −180°C

The frequencies 1145 and 1108 cm^{-1} of 2, 4-dichlorotoluene, 1135 and 1101 cm^{-1} of 3, 4-dichlorotoluene, and 1158 and 1098 cm^{-1} of 1, 2, 4-trichlorobenzene
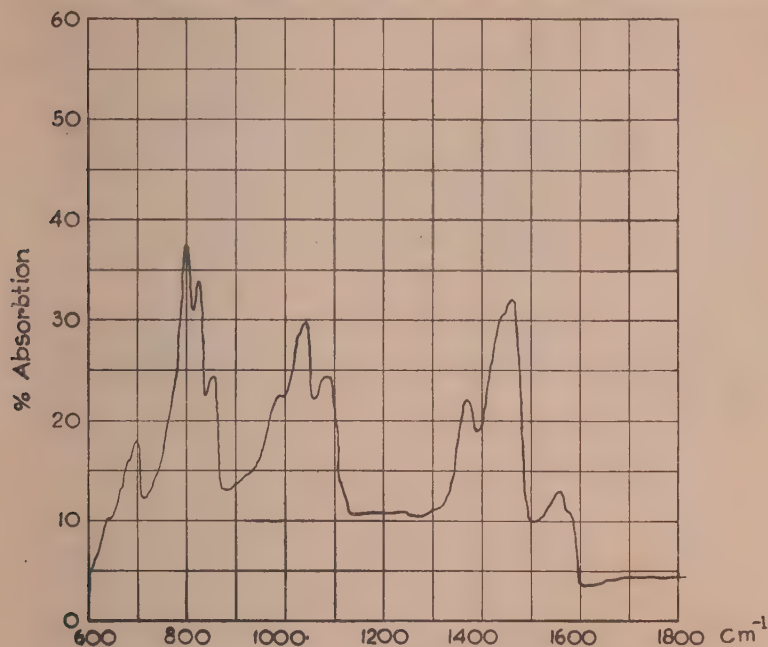

Fig. 3. Infrared spectrum of 2,4– dichlorotoluene (liquid at 26°C)

are probably due to a'-type vibration originating from e_{2g} and b_{2u} modes in benzene, the frequencies representing C—H in-plane deformation vibration. It may be noted that these lines are all polarised and the frequencies are only weakly active in the infrared. The Raman lines 1049, 1030 and 1052 cm^{-1} respectively of the two dichlorotoluenes and the trichlorobenzene may be due to a component of the e_{1u} (1035 cm^{-1}) mode of benzene.

As can be seen from the tables, that 2, 4- and 3, 4-dichlorotoluene and 1, 2, 4-trichlorobenzene show strong infrared bands at 1460, 1469 and 1459 cm^{-1} respectively, which are either absent or very weak in the Raman effect, and also bands at 1372, 1381 and 1376 cm^{-1} respectively. It is well known that within the methyl group in methyl substituted benzenes there are bands due to asymmetric and symmetric C—H bending oscillation falling in the 1450 and 1381 cm^{-1} regions. But the presence of strong bands at 1459 and 1376 cm^{-1} in the infrared spectrum of 1, 2, 4-trichlorobenzene clearly indicates that the similar frequencies observed in the dichlorotoluenes cannot be uniquely assigned to vibrations in the CH$_3$ group, for they may be due to some other suitable modes of vibration of the molecules themselves. From the discussions of previous workers, the 1460, 1469 and 1459 cm^{-1} bands due to the three compounds appear to represent a

component of the e_{1u} mode of frequency 1485 cm^{-1} in benzene. The frequencies 1372, 1381 and 1376 cm^{-1} may represent another component of the same mode. In the case of the dichlorotoluenes the bending modes of methyl group may be superposed on these frequencies. The bands near 1430 cm^{-1} due to the dichlorotoluenes may be attributed to a second component of the asymmetric bending in the methyl group usually observed in the methyl substituted compounds (Sheppard *et al*, 1953). The Raman lines 1592 cm^{-1} of 2, 4-dichlorotoluene, 1598 cm^{-1} of 3, 4-dichlorotoluene and 1591 cm^{-1} of 1, 2, 4-trichlorobenzene correspond in all probability to a component of e_{2g} mode in benzene of frequency 1596 cm^{-1}. The observed infrared frequencies are 1580, 1592 and 1566 cm^{-1} respectively, the other components in infrared are probably the frequencies 1558, 1564 and 1550 cm^{-1} respectively.

In all these three molecules with C_s symmetry, the 606 cm^{-1} e_{2g} vibration in benzene splits up into two a' components and these may be identified with
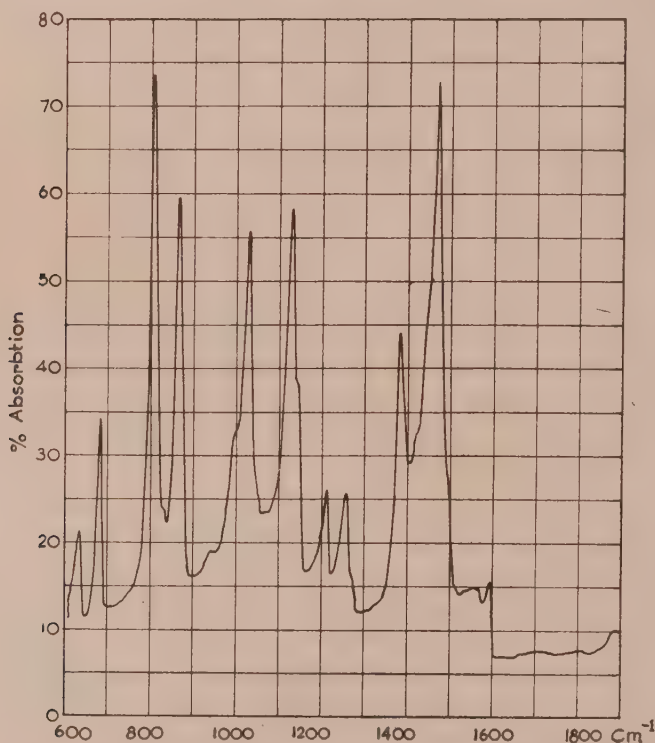

Fig. 4. Infrared spectrum of 3,4- dichlorotoluene (liquid at 26°C)

the polarised Raman lines 380 and 464 cm^{-1} of 2, 4-dichlorotoluene, 368 and 463 cm^{-1} of 3, 4-dichlorotoluene and 332 and 459 cm^{-1} of 1, 2, 4-trichlorobenzene.

In each case, the lower of the two frequencies would correspond to the mode in which all the atoms are displaced.

As discussed above, there are four bending modes in the plane of the benzene molecule viz., a_{2g} (1298 cm^{-1}), b_{2u} (1170 cm^{-1}), e_{2g} (1178 cm^{-1}) and e_{1u} (1035 cm^{-1}). These become a'-type vibrations in the case of C_s symmetry and are expected to give rise to frequencies corresponding to chlorine bending vibration. The three polarised Raman lines at 402, 435 and 395 cm^{-1} in the case of the three compounds may correspond to one such mode. At least another component of low frequency should be found near 200 cm^{-1} (Sponer and Kirby-Smith. 1941) but the deplorarisation of the observed lines in this region presents difficulty in assignment of this mode.

Out of the four hydrogen bending vibrations (a_{2u}, b_{2g}, e_{2u} and e_{1g}) perpendicular to the plane of the ring in benzene, there should result a'' type bending vibrations
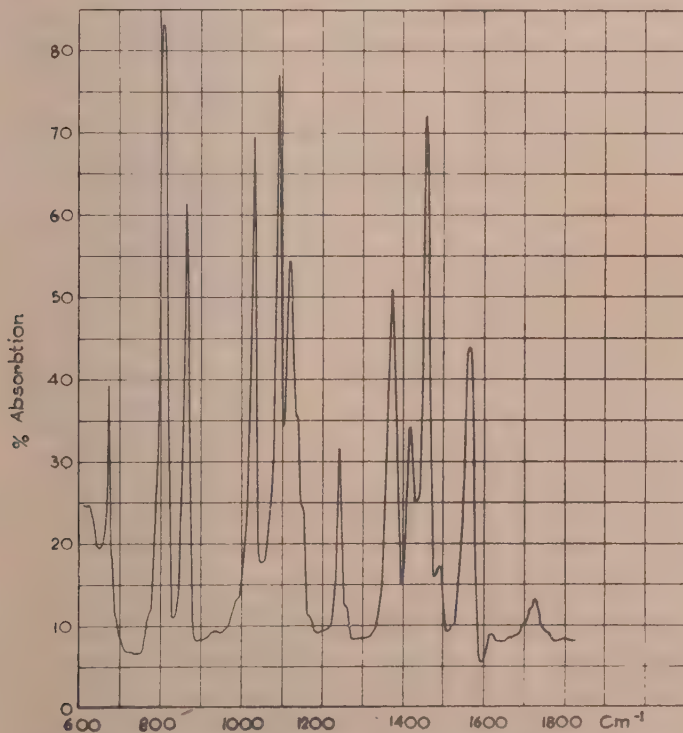

Fig. 5. Infrared spectrum of 1,2,4t- richlorobenzene (liquid at 26°C)

of hydrogen, chlorine and probably of methyl group, giving rise to depolarised Raman lines. It is known from previous results that 1, 2, 4-trisubstituted benzene compounds usually exhibit infrared band corresponding to a C—H out of plane deformation near 800 cm^{-1} (Bellamy, 1954). Accordingly, the bands 799, 805

and 810 cm $^{-1}$ observed in the infrared spectra of 2, 4-and 3, 4-dichlorotoluene and 1, 2, 4-trichlorobenzene may be taken to correspond to this vibration, but the absence of any corresponding Raman line in the case of all the three compounds is difficult to interpret as no line is expected to be forbidden in the Raman effect of compounds with C_S symmetry. The two depolarised low frequency Raman lines 181 cm,$^{-1}$ and 202 cm $^{-1}$ for 2, 4-dichlorotoluene, and 182 and 195 cm^{-1} for 1, 2, 4-trichlorobenzene correspond in all probability to components of out of plane chlorine bending modes. The value of 181 cm^{-1} is probably a little higher in the case of 3, 4-dichlorotoluene as is evident from the broadness of the 202 cm^{-1} line. Biswas (1958) has proposed the alternative assignment for line near 202 cm^{-1} observed in chlorotoluenes, that these may be due to dimeric type of associated molecules present in the liquid. This will be taken up while discussing the Raman effect at low temperatures. In both 2, 4- and 3, 4-dichlorotoluene, a depolarised line at 269 cm $^{-1}$ is observed, while there is no corresponding line in 1, 2, 4- trichlorobenzene. This may indicate that this frequency originates from a motion of the methyl group and we propose to associate it with $C-CH_3$ out of plane deformation.

The b_{2g} and e_{2u} modes of out of plane carbon vibration in benzene will produce a'' type vibrations giving depolarised Raman lines. One of the components of the e_{2u} mode which will be only slightly affected is probably the 312 cm^{-1} line in the dichlorotoluenes and 310 cm^{-1} in 1, 2, 4-trichlorobenzene. The other lower component may be detected in the 127 cm^{-1} line in the dichlorotoluenes and probably the 112 cm^{-1} line in 1, 2, 4- trichlorobenzene. The 645 cm^{-1} line may be the contribution of the b_{2g} mode.

In the Raman spectra of dichlorotoluenes two strong polarised lines at 834 and 870 cm^{-1} have been observed (825 and 865 cm^{-1} in the infrared). These may be a' vibration originating from a_{1g}, b_{1u}, e_{2g} and e_{1u} modes in benzene, though it is difficult to propose any definite interpretation of these bands.

(b) *Changes in the intramolecular oscillations of* 2, 4- *and* 3, 4-*dichlorotoluene in the solid state at* $-180°C$.

In the Raman spectra of both 2, 4- and 3, 4-dichlorotoluene a line at 127 cm^{-1} is observed which is found to disappear in the spectra of the solids. Further, in the case of 2, 4-dichlorotoluene the 181 cm^{-1} line is also absent and a new line at 160 cm $^{-1}$ is observed at $-180°C$. In the case of 3, 4-dichlorotoluene the broad band at 202 cm $^{-1}$ becomes sharp while a new line at 145 cm^{-1} appears when the compound is solidified. These changes probably indicate that in the solid state at $-180°C$, the molecules of the compounds become associated resulting in restriction of some vibrations of the single molecules. This probably causes the $C-Cl$ out of plane bending vibration of frequency 181 cm $^{-1}$ in the case of 2, 4-dichlorotoluene and one component of the mode of frequency 202 cm^{-1} of 3, 4-dichlorotoluene to shift

to lower energies and the lower component of C–C out of plane deformation vibration of frequency 127 cm^{-1} to disappear. The absence of any appreciable shift of the 202 cm^{-1} line due to 2, 4-dichlorotoluene and the other component of 202 cm^{-1} line due to 3, 4-dichlorotoluene may be due to the fact that these lines have their origin in a motion of dimeric molecules present in the liquid state as proposed by Biswas (1958) in the case of monochlorotoluenes.

When 2, 4-dichlorotoluene is solidified and cooled to –180 C the lines 312, 646 and 1204 cm^{-1} are shifted to 318, 653 and 1210 cm^{-1} respectively without any appreciable changes in the relative intensity. Thus the component of C–C out of plane deformation vibrations of frequencies 312 and 646 cm^{-1} which are largely unaffected by substitution are found to be only slightly influenced by association of the molecules in the solid state. In the case of 3, 4-dichlorotoluene, the lines 686 and 1030 cm^{-1} are shifted to 680 and 1026 cm^{-1} respectively. Further, the strong line at 1135 cm^{-1} splits up into two lines at 1146 and 1170 cm^{-1} respectively. It is also observed that the relative intensities of lines 1592 and 2926 cm^{-1} of 2, 4-dichlorotoluene and 1598 and 2938 cm^{-1} of 3, 4-dichlorotoluene are reduced in the solid state at –180 C. The diminution in intensity of the lines of frequencies 1592 and 1598 cm^{-1} due to a mode involving stretching of the C = C bond may indicate that in the case of both these molecules formation of associated groups takes place at the expense of the C = C bond.

(c) *Low frequency Raman lines in 2, 4- and 3, 4-dichlorotoluene*

In the solid state at –180 C, the 2,4-dichlorotoluene exhibits Raman lines at 28, 42, 84 and 101 cm^{-1} in the low frequency region, the lines at 28 and 84 cm^{-1} being relatively stronger. On the other hand, 3, 4-dichlorotoluene under similar condition yields only two low frequency Raman lines at 46 and 76 cm^{-1} respectively. Probably the number of types of associated groups in the case

TABLE IV

Luminescence spectra of 2, 4- and 3, 4-dichlorotoluene in the solid state at –180° C

2, 4-Dichlorotoleune at –180°C		3, 4-Dichlorotoluene at –180°C	
Position of bands in cm^{-1} and Intensity	Separation in cm^{-1} from the first band	Position of bands in cm^{-1} and Intensity	Separation in cm^{-1} from the first band
22717 (ms)	0	24180 (w)	0
21197 (ms)	1520	22556 (s)	1632
		21197 (ms)	2983
		20889 (ms)	3291

of 3, 4-dichlorotoluene is smaller than that in 2, 4-dichlorotoluene because of proximity of the chlorine atoms in the 3- and 4 positions in the former molecule.

(d) *Luminescence spectra of 2, 4- and 3, 4- dichlorotoluene at* $-180°C$

When 2, 4-dichlorotoluene is frozen and cooled to $-180°C$, two strong and very broad luminescence bands with centres at about 22717 and 21197 cm^{-1} are observed and the separation 1520 cm^{-1} between the components approximates to C = C vibrational frequency. In the case of 3, 4-dichlorotoluene, four broad bands are observed at 24180, 22556, 21197 and 20889 cm^{-1} respectively. The separation of the last three bands from the first one are 1632, 2983 and 3291 cm^{-1} respectively. In this case also the C = C vibration is prominent as the 1632 cm^{-1} frequency, the 3291 cm^{-1} frequency being approximately the first harmonic of 1632 cm^{-1}. The other frequency separation 2983 cm^{-1} may represent a C—H valence oscillation. It may be mentioned here that in the case of other chloro and bromo substituted toluenes, Biswas (1954, 1955) and Sanyal (1953) observed similar broad luminescence bands with a frequency separation approximating to C = C vibrational frequency. Further, in all these compounds the associated groups in the solid state at $-180°C$ are apparently formed at the expense of the C = C bond as is evident from diminution in intensity of this vibrational frequency at the low temperature. It is, therefore, interesting to note that this particular mode is coupled with the electronic transition giving rise to the luminescence spectra exhibited by these compounds in the solid state at low temperature.

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ULTRASONIC VELOCITY IN SOME AQUEOUS SOLUTIONS OF ELECTROLYTES

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ABSTRACT. The variation of ultrasonic velocity, adiabatic compressibility, apparent molal compressibility and molar sound velocity with concentration is studied in eleven electrolyte solutions. The results are interpreted in the light of Debye-Hückel's theory of electrolytes. The hydration numbers are estimated for all the electrolytes and compared with the data obtained by other methods. Non-linear variations of molar sound velocity with molar concentration observed in some cases is explained in terms of molecular association and ionic solvation.

1. INTRODUCTION

Ultrasonic velocity measurements in electrolytic solutions are of considerable importance as they enable us to test the validity of the several theories of electrolyte solutions. Besides it has been possible to estimate the number of water molecules attached to the ions in solution known as hydration number. Following the theory of Debye-Hückel, Gucker (1933) has derived certain limiting laws for the apparent molal compressibility and interpreted his experimental data in the light of this theory. Subsequently Bachem (1936), Scot, Obenhaus and Wilson (1934), Krishnamurty (1950), Rao and Rao (1958) studied the apparent molal compressibilities in several solutions of electrolytes of different valence types and reported deviations from the limiting laws. While studying variations of ultrasonic velocities in solutions of electrolytes certain unusual features like decrease of velocity with increase of concentration have also been reported by some investigators in a few electrolytes namely, potassium iodide, lead nitrate, lead acetate and uranyl acetate. Very recently, Marks (1960) has calculated the hydration numbers for salts of alkali metals investigated by him.

As very little work has been done particularly on the estimation of hydration numbers and molar sound velocities in the case of solutions of electrolytes, the authors have taken up this investigation by taking measurements for about eleven new electrolytes.

2. RESULTS

Aqueous solutions of the following salts are studied.

1. Lithium acetate.
2. Sodium acetate.
3. Potassium acetate.
4. Cobaltous acetate.
5. Cadmium acetate
6. Cadmium chloride.
7. Cadmium Bromide
8. Strontium Bromide.
9. Barium bromide.
10. Cadmium Iodide.
11. Zinc Iodide.

The salts used are of either E. Merck or B. D. H. Solutions of different concentrations are prepared and the ultrasonic velocities are determined by a fixed path variable frequency interferometer accurate to ± 1 m/sec. The densities (ρ) are determined by specific gravity bottle using a Bunge balance accurate to 1 mgm.

The values of adiabatic compressibility β and apparent molal compressibility $\phi(k_2)$ are calculated by using the relations

$$\beta = \frac{1}{\rho V^2}, \quad \phi(k_2) = \frac{\beta \times 1000}{C} - \frac{\beta_1}{d_1}\left(\frac{1000d}{C} - M\right)$$

Where β_1 is the adiabatic compressibility of the solvent, C = Molar concentration and M = the molecular weight of the solute.

The variation of ultrasonic velocity, adiabatic compressibility and apparent molal compressibility with concentration for all the eleven salts investigated is shown graphically in Figs. 1 to 6.
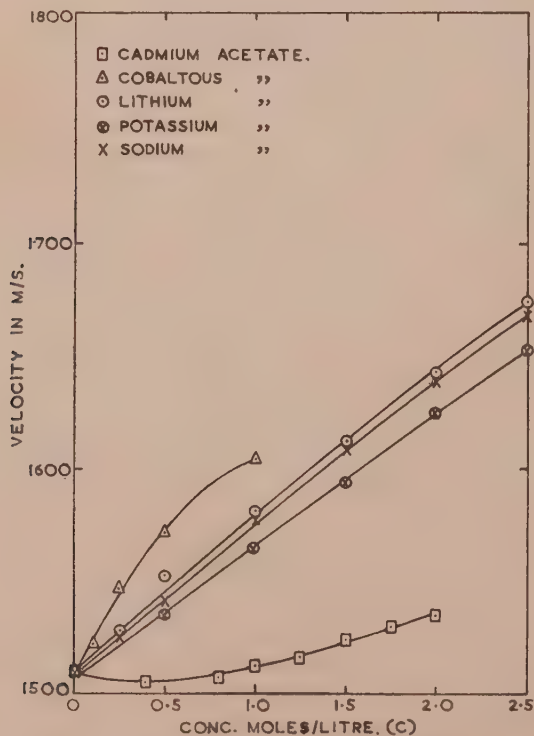

Fig. 1. Variation of ultrasonic velocity with concentration of the electrolyte.
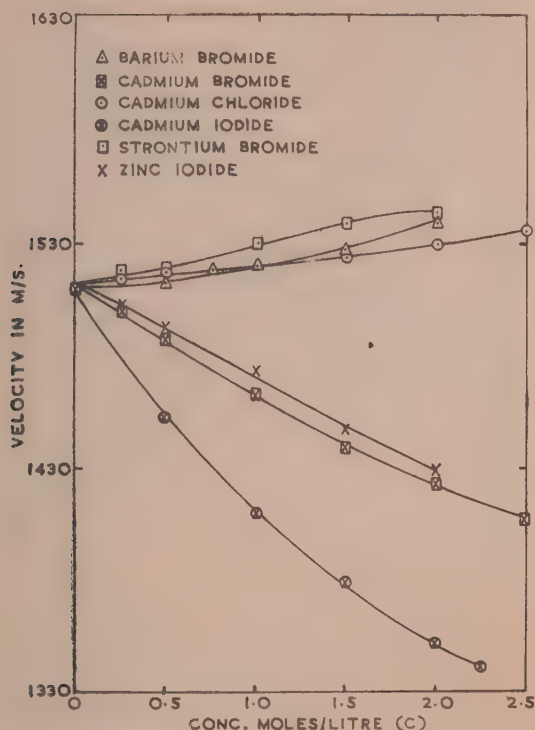
FIG. 2. Variation of ultrasonic velocity with concentration of the electrolyte.

VARIATION OF ULTRASONIC VELOCITY AND ADIABATIC COMPRESSIBILITY WITH CONCENTRATION

It can be seen from Figs. 1 and 2 that in almost all the salts studied, the velocity is found to increase with concentration except in the cases of zinc iodide, cadmium bromide and iodide. Cadmium acetate solution showed a slight decrease in velocity initially and then showed gradual increase with concentration almost linearly. Although the anomalies of decrease of velocity with increase of concentration are noticed for these four salts, the adiabatic compressibility always showed the normal decrease with increase of concentration as can be seen in Figs. 3 and 4. The non-linear variation of velocity with concentration in the case of cobalt acetate is similar to the non-linear variation exhibited by some ferrous salts. A comparative study of the behaviour in the case of cadmium halides shows that the gradient of velocity-concentration graph decreases progressively from cadmium chloride to iodide. In a similar manner the velocities for barium bromide solutions are lower than those of barium chloride solutions studied by
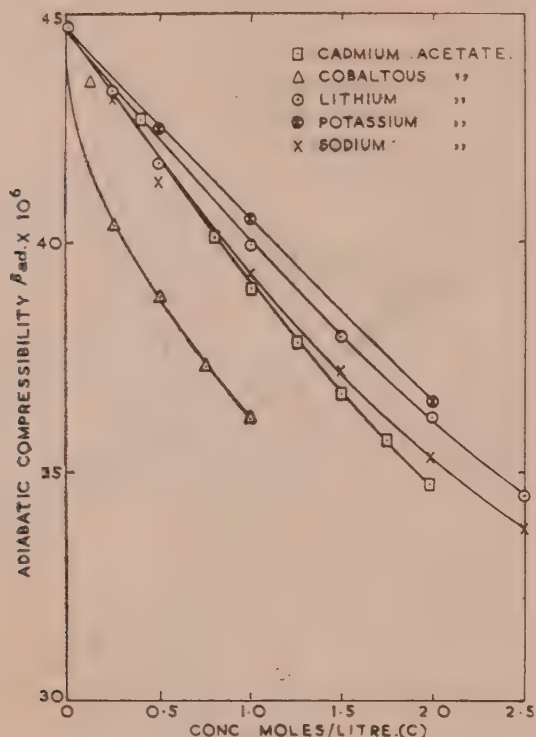
FIG. 3. Variation of adiabatic compressibility with concentration of the electrolyte.

Bachem (1936). It appears from these observations that for a fixed positive radical increase of atomic weight of the negative radical in the halogen group decreases the ultrasonic velocity. This is also borne out by data available for alkali halides studied by earlier works (Bachem. 1936; Krishnamurty, 1950 and Wada *et al.*, 1950).

It may also be noted that solutions of all the iodides studied so far show a decrease of velocity with concentration at first and later on show an increase in some cases.

The compressibility is always found to decrease with increase of concentration following closely the equation.,

$$\beta = \beta_1 + AC + BC^{3/2}$$

given by Gücker (1933).

From a systematic study of a series of aqueous solutions of some sulphates Marks (1944) has drawn the important conclusion that for a fixed anion the com-
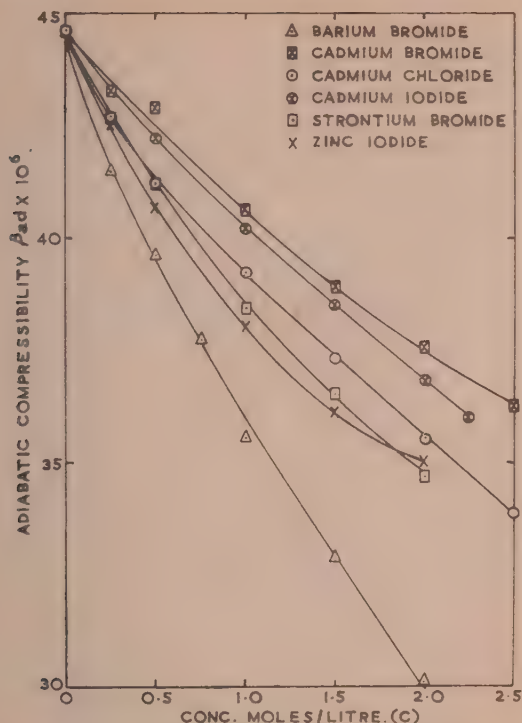
FIG. 4. Variation of adiabatic compressibility with concentration of the electrolyte.

pressibility at a particular concentration decreases with increasing ionic radius of the cation. Here an attempt is made to interpret the results of this investigation in the light of this rule. For this purpose the data available in literature are also utilised. The compressibility data for different electrolyte solutions at a fixed concentration either 0.5 M to 1.0 M are presented in Table I.

Comparing the sodium-flouride, chloride and nitrate solutions with the corresponding potassium salt solutions for the same concentration it is seen that the compressibility of the potassium salt solutions is always less. This may be attributed to the higher radius of K^- ion compared to Na^- ion. Comparing the adiabatic compressibilities of 1M solutions of $MgCl_2$, $CaCl_2$, $CdCl_2$ it is seen that $CdCl_2$ and $CaCl_2$ obey the above rule while $MgCl_2$ shows deviation from it. This deviation may be due to the partial hydrolysis of magnesium chloride into magnesium hydroxide. All the three bromide solutions studied follow this rule quite well. The two iodides of zinc and cadmium show deviation from this rule. Similar deviations are noticed in the case of nitrates and sulphates of Fe. Co. Ni which hydrolyse in aqueous solutions. It is obvious that the effect of water of

TABLE I

Salt	Formula		Conc. Moles/litre	$\beta \times 10^{12}$ Cm²/dyne	Ionic radius of the Å catio
Sodium fluoride	NaF	(1-1)	0.5	42.14	0.95
Potassium fluoride	KF	(1-1)	0.5	39.43	1.33
Sodium chloride	NaCl	(1-1)	1.0	38.02	0.95
Potassium chloride	KCl	(1-1)	1.0	36.46	1.33
Magnesium chloride	$MgCl_2$	(2-1)	1.0	35.70	0.65
Calcium chloride	$CaCl_2$	(2-1)	1.0	36.50	0.99
Cadmium chloride	$CdCl_2$	(2-1)	1.0	39.37	0.97
Sodium nitrate	$NaNO_3$	(1-1)	0.5	41.73	0.95
Potassium nitrate	KNO_3	(1-1)	0.5	41.03	1.33
Strontium nitrate	$Sr(NO_3)_2$	(2-1)	0.3	41.01	1.13
Barium nitrate	$Ba(NO_3)_2$	(2-1)	0.3	40.52	1.35
Nickel nitrate	$Ni(NO_3)_2$	(2-1)	0.3	41.80	0.69
Barium bromide	$BaBr_2$	(2-1)	1.0	35.96	1.35
Strontium bromide	$SrBr_2$	(2-1)	1.0	38.59	1.13
Cadmium bromide	$CdBr_2$	(2-1)	1.0	39.88	0.97
Zinc Iodide	ZnI_2	(2-1)	1.0	37.27	0.74
Cadmium iodide	CdI_2	(2-1)	1.0	39.46	0.97
Magnesium sulphate	$MgSO_4$	(2-2)	0.5	36.77	0.65
Zinc sulphate	$ZnSO_4$	(2-2)	0.5	36.34	0.74
Iron sulphate	$FeSO_4$	(2-2)	0.5	38.80	0.75
Lithium acetate	$Li(CH_3COO) 2H_2O$	(1-1)	1.0	39.15	0.60
Sodium acetate	$Na(CH_3COO)3H_2O$	(1-1)	1.0	38.54	0.95
Potassium acetate	$K(CH_3COO)$	(1-1)	1.0	39.77	1.33
Cadmium acetate	$Cd(CH_3COO)_2 2H_2O$	(2-1)	1.0	38.32	0.97
Cobaltous acetate	$Co(CH_3COO)_2 4H_2O$	(2-1)	1.0	35.52	0.72

hydration is to decrease the compressibility of the solution. If we however compare the three salts lithium, sodium and cadmium acetates having nearly the same number of molecules of water of crystallization, it will be seen that the compressibility decrease from lithium to cadmium where as the ionic radius increases from Li^+ to Cd^{++} progressively. The deviation from this rule observed in the case of cobaltous acetate may be partly due to hydrolysis and partly due to the large
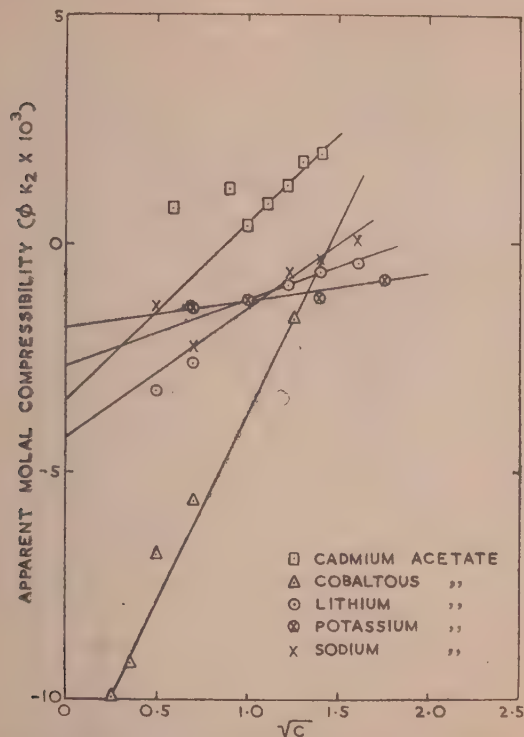
FIG. 5. Relation between apparent molal compressibility and squareroot of concentration.

number of molecules of water of crystallisation, the high value of compressibility for solutions of potassium acetate compared to others inspite of its large ionic radius of 1.33 may be attributed to the lack of water of crystallisation.

APPARENT MOLAL COMPRESSIBILITIES AND ESTIMATION OF HYDRATION NUMBERS

It can be seen from Figs. 5 and 6 that the apparent molal compressibility $\phi(k_2)$ varies almost linearly with square root of concentration in all cases except cadmium salts for which deviations are noticed particularly at lower concentrations. The values of $\phi(k_2)$ for most of the salt solutions are generally negative and there are very few cases for which positive values are reported. In this investigation positive values of $\phi(k_2)$ are observed for the case of cadmium acetate, bromide and Iodide and strontium bromide solutions. The values of the gradients

$\dfrac{\partial \phi(k_2)}{\partial \sqrt{c}}$ are determined and presented in Table II along with the theoretically computed values.
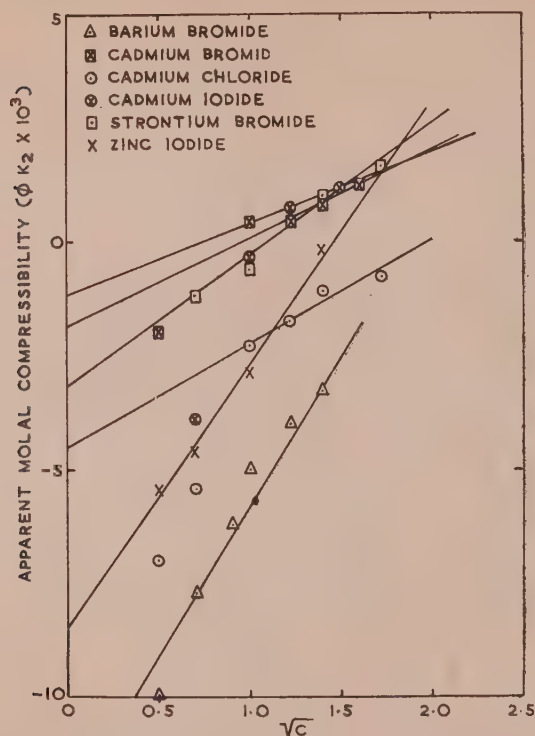
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FIG. 6. Relation between apparent molal compressibility and square root of concentration.

TABLE II

Salt	Type of Electrolyte	$(\varepsilon v_i z_i^2)^{3/2}$	$\{\partial\phi(k_2)/\partial c^{1/2}\}$		$(K_2) \times 10^3$ $c=0$	Hydration number
			10^{10} C.G.S. Theoretical	10^4 Expt.		
Lithium acetate $2H_2O$	1-1	2.828	6.3	29.50	−2.90	3.60
Sodium acetate $3H_2O$	1-1	2.828	6.3	23.00	−3.55	4.40
Potassium acetate	1-1	2.828	6.3	12.50	−3.30	4.20
Cadmium acetate $2H_2O$	2-1	14.700	32.6	40.00	+3.50	4.40
Cabaltous acetate $4H_2O$	2-1	14.700	32.6	110.00	−22.90	28.50
Barium bromide	2-1	14.700	32.6	67.44	−12.20	15.40
Strontium bromide	2-1	14.770	32.6	15.80	−3.66	4.50
Cadmium bromide	2-1	14.700	32.6	43.00	−0.80	—
Cadmium iodide	2-1	14.700	32.6	34.00	−0.38	—
Cadmium chloride	2-1	14.700	32.6	26.66	−5.00	6.20
Zinc iodide	2-1	14.700	32.6	62.10	−9.18	1.40

In the (1—1) type electrolytes studied the slopes of almost all the solutions show deviations from the theoretical values but it is found that the experimental values are always higher. There is a fairly good agreement between experimental and theoretical values in the case of the (2—1) type salts cadmium acetate, bromide and iodide although these solutions showed unusual behaviour in other physical properties. Although strontium bromide and cadmium chloride belong to (2—1) valence type, their gradients are even smaller than the theoretical values of the (1—1) type electrolyte solutions. In general, it may be concluded from the above study of the apparent molal compressibilities that Gücker's limiting law is only in qualitative agreement with the experimental values.

It is well known that the water molecules in the immediate neighbourhood of ions in an electrolyte solution are intimately bound to the ions. This process is known as hydration. The first layer of water molecules attached to the ion is known as primary water of hydration. Estimation of primary hydration numbers of ions is now possible by several methods based on diffusion, ionic mobilities, activity coefficients etc. Hydration numbers can also be estimated from a study of apparent molal compressibility on the assumption that the ion as well as the primary water of hydration are incompressible compared to the free solvent molecules. Wada and Shimbo (1950) have given the following relation from which the hydration number can be calculated

$$\underset{c \to 0}{\text{Lin}} \quad \phi(k_2) = -\beta_1 V_h$$

V_h is the volume of primary water of hydration for more of the electrolyte. The limiting value $\underset{c \to 0}{\phi(k_2)}$ can be obtained by extrapolating $\phi(k_2)$ versus $\sqrt{c}$ graph to zero concentration. Using the experimental values of $\underset{c \to 0}{\phi(k_2)}$ and β_1 the values of V_b are estimated. By making the further assumption that the molar volume of the solvent molecules in the primary hydration sheath is the same as that of the pure solvent, the combined primary hydration number for the electrolyte is obtained by dividing V_h by the molar volume of water. The experimental values thus obtained for all the electrolytes investigated are presented in the last column in Table II. The values of hydration numbers of lithium, sodium and potassium acetates are nearly of the same order of magnitude as the values 4, 5 and 5 for the ions Le^+, Na^+ and K^+ respectively available in literature (Bell, 1958). This leads to the conclusion that the contribution due to the acetate radical is very low. The low values of 4.4 obtained for cadmium acetate shows that the hydration number of Cd^{++} ion is of the same order as Na^+ or K^+ ions although it is doubly ionised. Assuming the contribution of Cl^- ion to combined hydration number as unity as obtained from activity coefficients method, it will be seen that the data for $CdCl_2$ leads to the same value of about 4 for the primary hydration number

of Cd^{++} ion. The abnormally low values of hydration number obtained for $CdBr_2$ and CdI_2 may be attributed to the anomalous variation of ultrasonic velocity with concentration and the non-linear nature of $\phi(k_2)$ versus $c^{\frac{1}{2}}$ plot. Cobaltous acetate gives an abnormally high value of 28.5 for the hydration number part of which may be due to hydrolysis. Taking the value for bromine as one, the hydration number for Sr comes out to be approximately 4 which is of the same order as Na^+ or K^+ ions. Similarly, the values obtained for Ba^{++} and Zn^{++} ions are 13 and 9 respectively.

## MOLAR SOUND VELOCITY AND ASSOCIATION

Rao (1940) has shown that the molar sound velocity R given by $\dfrac{M}{\rho}\,(V)^{1/3}$ is independent of temperature for non-associated liquids. For associated liquids like water and alcohol, R varies appreciably with temperature and Weissler has utilised this variation for studying the change of relative association with temperature. It is well known that in the case of ideal solutions where there is no association or complex formation, the R value for the solution estimated by using the relation

$$R = \frac{\bar{M}}{\rho}\,(V)^{1/3}$$

where
$$\bar{M} = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2}\,, \qquad C_m = \frac{n_1}{n_1 + n_2}$$

varies linearly with molar concentration of the solute C_m from the value of R for the solvent to that of the solute. The theoretically computed values of R from the known molar sound velocity increments for the atoms may be taken to be equal to the values for the ideal solution. The R values for the various solutions investigated are computed and it is found that the R variation with molar fraction is nearly linear in all cases except cadmium halides. It is also found that the computed values of R for the solutions are always higher than the theoretically experimental values. Taking the ratio K of computed to experimental value of R as an index of the degree of association and solvation, these values are plotted against molar fraction C_m as shown in Fig. 7. The value of $K = 1.253$ obtained for zero concentration gives an idea of the degree of association in pure water which is responsible for the lowering of R. In the presence of an electrolyte the water molecules will be dissociated, consequently there will be a decrease in the value of R. Simultaneously there is also the phenomenon of solvation which increases the value of K. In all the acetates studied K decreases with increase of concentration showing a decrease of association of water molecules with concentration. In the case of aqueous solutions of cadmium chloride
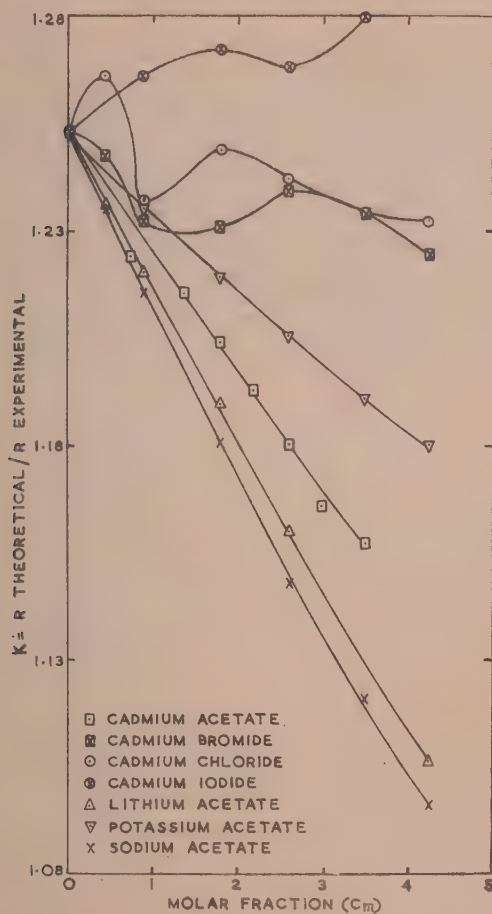
Fig. 7. Variation of "K" factor with molar fraction "C_m".

bromide and iodide peculiar variations of the factor K are observed. The curves show maxima and minima indicating that the process involved is quite complex. This effect is particularly predominant in the case of cadmium iodide for which the K factor continuous to increase with concentration, a feature which is quite unusual.

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DIPOLE MOMENT AND RELAXATION TIME OF CERTAIN TRI-SUBSTITUTED BENZENES

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ABSTRACT. Using the author's method, dipole moment and relaxation time are determined for six tri-substituted benzenes from measurements at 3.26 cms. Benzene is used as the solvent.

In a previous paper (Sobhandri, 1960), the author has described a method for evaluating relaxation times and dipole moments of certain polar molecules in dilute solution from measurements of the dielectric constant ϵ' and loss factor ϵ'' at a single frequency. This method is adopted in this paper for determining τ and μ of six tri-substituted benzenes for which no data are available in the literature. Benzene is used as the solvent. The experimental procedure was the same as the one described in an earlier paper (Narasimha Rao, 1956) from this laboratory. ϵ' and ϵ'' are calculated using the standing wave method of Roberts and von Hippel (1946).

Tables I to VI give the values of ϵ' and ϵ'' for different weight fractions along with the values of $\dfrac{\epsilon''}{\epsilon'-\epsilon_\infty}$. The mean value of $\dfrac{\epsilon''}{\epsilon'-\epsilon_\infty}$ is taken to calculate the relaxation time and the dipole moment. The final values of τ and μ are collected in Table VII.

All the molecules investigated may be taken as rigid and approximately spherical since they are formed by nuclear substitution in the benzene ring. The first four molecules (the toluenes) are of the same molecular weight, the main difference among themselves being in the location of the different groups. The other two are similar.

The dipole moment values obtained agree well with the r.f. values determined by Narasimha Rao (1956). Though the values of τ are almost of the same order for the four toluenes, a slight increase with increasing μ is evident. A similar feature may also be seen in the case of the other two nitrobenzenes. However, both μ and τ are considerably higher in the nitro compounds than in the toluenes.

TABLE I
6-Chloro 3-nitrotoluene
$$\epsilon_1 = 2.270$$

S.NO.	W	ε'	ε''	$\dfrac{\varepsilon''}{\varepsilon' - \varepsilon_1}$
1	0.005578	2.296	0.01863	0.7164
2	0.006988	2.298	0.02141	0.7645
3	0.008614	2.300	0.02418	0.8060
4	0.010600	2.304	0.02828	0.8296
5	0.012590	2.314	0.03028	0.6880

Mean $\dfrac{\varepsilon''}{\varepsilon' - \varepsilon_1} = 0.7609$

$\tau = 13.19 \times 10^{-12}$ Sec. $\mu = 3.09$ D

TABLE II
2-Chloro 4-nitrotoluene
$$\epsilon_1 = 2.270$$

S.NO.	W	ε'	ε''	$\dfrac{\varepsilon''}{\varepsilon' - \varepsilon_1}$
1	0.004501	2.299	0.02443	0.8424
2	0.005178	2.301	0.02731	0.8810
3	0.007437	2.312	0.03598	0.8569
4	0.009552	2.322	0.04612	0.8869
5	0.010610	2.327	0.05110	0.8964

Mean $\dfrac{\varepsilon''}{\varepsilon' - \varepsilon_1} = 0.8727$

$\tau = 15.14 \times 10^{-12}$ Sec. $\mu = 4.17$ D

TABLE III
6-Chloro 2-nitrotoluene
$$\epsilon_1 = 2.270$$

S.NO.	W	ε'	ε''	$\dfrac{\varepsilon''}{\varepsilon' - \varepsilon_1}$
1	0.006063	2.294	0.01782	0.7425
2	0.007230	2.300	0.02065	0.6885
3	0.008710	2.304	0.02367	0.6961
4	0.10680	2.310	0.02855	0.7137
5	0.11650	2.316	0.03341	0.7261

Mean $\dfrac{\varepsilon''}{\varepsilon' - \varepsilon_1} = 0.7134$

$\tau = 12.37 \times 10^{-12}$ Sec. $\mu = 3.11$ D

TABLE IV
4-Chloro 2-nitrotoluene
$$\epsilon_1 = 2.270$$

S.NO.	W	ϵ'	ϵ''	$\dfrac{\epsilon''}{\epsilon' - \epsilon_1}$
1	0.005089	2.296	0.02011	0.7734
2	0.006531	2.304	0.02745	0.8074
3	0.007396	2.310	0.02928	0.7319
4	0.009208	2.317	0.03671	0.7811
5	0.011480	2.329	0.04640	0.7863

Mean $\dfrac{\epsilon''}{\epsilon' - \epsilon_1} = 0.7760$

$\tau = 13.46 \times 10^{-12}$ Sec. $\mu = 3.66$ D

TABLE V
2, 3-Dichloro nitrobenzene
$$\epsilon_1 = 2.270$$

S.NO.	W	ϵ'	ϵ''	$\dfrac{\epsilon''}{\epsilon' - \epsilon_1}$
1	0.00743	2.310	0.03698	0.9458
2	0.01040	2.319	0.04704	0.9601
3	0.01291	2.322	0.05070	0.9750
4	0.01614	0.327	0.05546	0.9729
5	0.01893	2.341	0.06963	0.9806

Mean $\dfrac{\epsilon''}{\epsilon' - \epsilon_1} = 0.9669$

$\tau = 16.77 \times 10^{-12}$ Sec. $\mu = 3.82$ D

TABLE VI
2, 5-Dichloro nitrobenzene
$$\epsilon_1 = 2.270$$

S.NO.	W	ϵ'	ϵ''	$\dfrac{\epsilon''}{\epsilon' - \epsilon_1}$
1	0.008802	2.306	0.0320	0.8896
2	0.01030	2.311	0.0367	0.8960
3	0.01239	2.316	0.0441	0.9588
4	0.01601	2.325	0.0532	0.9674
5	0.1893	2.329	0.0549	0.9309

Mean $\dfrac{\epsilon''}{\epsilon' - \epsilon_1} = 0.9286$

$\tau = 16.11 \times 10^{-12}$ Sec. $\mu = 3.41$ D

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TABLE VII
Temperature 28°C

Substance	$\tau \times 10^{12}$ sec.	μ	$\mu_{r.f.}$D
6-Chloro 2-nitrotoluene	12.37	3.11	2.93
6-Chloro 3-nitrotoluene	13.19	3.09	3.11
4-Chloro 2-nitrotoluene	13.46	3.66	3.63
2-Chloro 4-nitrotoluene	15.14	4.17	4.05
2, 5-Dichloro nitrobenzene	16.11	3.41	3.45
2, 3-Dichloro nitrobenzene	16.77	3.82	3.86

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ON THE SINGLET → TRIPLET ABSORPTION IN AROMATIC COMPOUNDS IN GASEOUS STATE

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(Received, November 4, 1960)

Plate IX

ABSTRACT.   The absorption spectra in the near ultraviolet region of benzene and *o*-bromotoluene in the vapour state at the respective saturation pressures at the room temperature with a path length of about 62 feet have been photographed and compared with the spectra due to the substances in the liquid state having equivalent path lengths. It has been observed that although benzene in the liquid state with a path length 1.2 cms shows considerable absorption in the 3300Å – 3400Å region due to singlet→triplet transition, such absorption in the case of the vapour at 12 mm pressure, with a path length of 62 feet is very much less than that in the liquid. Similar results have been observed in the case of *o*-bromotoluene, the path length being 7 mm for the liquid and 62 feet for the vapour at 55 mm pressure. It has been pointed out that the singlet → triplet absorption and the corresponding luminescence observed by previous workers in these cases are enhanced considerably in the state of aggregation of the molecules.

INTRODUCTION

The singlet→triplet absorption in some aromatic liquids was first observed by Lewis and Kasha (1945). Kasha also observed later (Kasha, 1952) that this absorption is strengthened when a heavy substituent atom is introduced in the benzene molecule and also when the molecules are dissolved in a solvent, the molecules of which contain such heavy atoms. Sirkar and Biswas (1956) and Biswas (1956) observed that the relative intensities of the bands and their positions in the luminescence spectra of frozen solutions of certain disubstituted benzene compounds depend to some extent on the nature of the solvent. Later, Roy (1959) proved conclusively that the luminescence in such cases was produced after absorption in the process of singlet→triplet transition. As it was suggested by Sirkar and Biswas (1956) and also by Biswas (1956) that the luminescence exhibited by the molecules in the solid state at low temperatures might be due to formation of small groups of molecules it would be of interest to find out whether the singlet→triplet absorption is an intrinsic property of the individual molecules in the gaseous state or it is developed in the state of aggregation. It is difficult to make experimental arrangement for this purpose, because the life time of the

triplet state is large and consequently the absorption is very weak. However, the absorption is exhibited by some of these liquids even when the absorbing path is only about 5 cms. If the absorption could be detected in these cases using absorption cells of thickness about 1 cm, it would be possible to study the absorption in the vapour with equivalent path length.

An attempt has, therefore, been made to study the absorption spectra in the near ultraviolet region of vapours of benzene and *o*-bromotoluene at pressures 12 cm and 5.5 cm respectively, the absorbing path being 18.90 metres long in each case. The spectra due to the liquids of equivalent thickness have also been photographed under identical conditions and compared with those due to the vapours. The results have been discussed in the present paper.

EXPERIMENTAL

The absorbing path of the vapour about 18.90 metres long was obtained by making two cells of straight pyrex glass tubes each about 32 feet long, provided with quartz windows and placed side by side parallel to each other. The continuous radiation from a tungsten filament lamp in glass bulb was made parallel with a quartz lens and passed through one of the tubes. The rays being then reflected by two right angled quartz prisms, passed through the other tube and were finally focussed on the slit of the spectrograph with another quartz lens. The radiation emitted by the lamp was found to have wavelengths longer than $3000\,\text{Å}$ and therefore the absorption due to singlet$\rightarrow$ singlet transition was not possible in this arrangement. A bulb of Pyrex glass containing the liquid was connected to each of the absorption cells through a greaseless stopcock and a side tube. First, the long cells were evacuated and the spectrum of the incident radiation passing through the tubes was recorded. The short empty cell for the liquid was next placed in the path of the rays and the long absorption cells were filled with the vapour of the liquid at the saturation pressure which was measured with a differential manometer. The pressure was found to be 120 mm in the case of benzene and 55 mm in the other case. After photographing the absorption spectrum of the vapour on a photographic film the long cells were evacuated and the short cell was filled with the distilled liquid and the absorption spectrum of the liquid was photographed on the same film with the same exposure and under identical conditions as in the case of the vapour.

The liquids benzene and *o*-bromotoluene used in the investigation were of chemically pure quality and they were first fractionated and then distilled in vacuum before being introduced in the bulb mentioned above. The thickness of the cell for the liquid was 1.2 cm for benzene and 7 mm in the case of *o*-bromotoluene. The spectra were photographed with Hilger medium quartz spectrograph on Agfa Isopan films, the time of exposure being about 10 hours in each case.
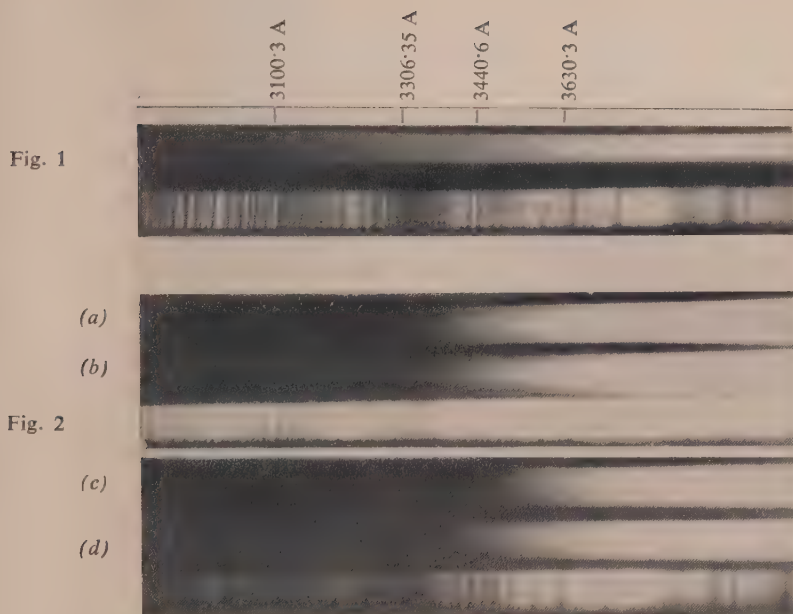
Ultraviolet absorption spectra

Fig. 1.   Absorber — evacuated cell, 18·90 metres long

Fig. 2.   (a)   Absorber — benzene (liquid), 12 mm long cell
                    + above evacuated cell
          (b)   Absorber — benzene vapour at 120 mm of Hg,
                    18·90 metres long cell
          (c)   Absorber — o-bromotoluene (liquid), 7·0 mm long cell
                    + above evacuated cell
          (d)   Absorber — o-bromoluene vapour at 55 mm of Hg,
                    18·90 metres long cell

RESULTS AND DISCUSSION

The spectrograms for benzene and *o*-bromotoluene are reproduced in Figs. 2(a), 2(b), 2(c) and 2(d) in Plate IX, the spectrum of the incident continuous radiation passing through the evacuated absorption tube being shown in Fig. 1. These spectra show that in the case of benzene in the vapour state (Fig. 2b) there is only a very weak absorption in the region 3400 Å-3300 Å, while in the spectrum due to the liquid of equivalent thickness (Fig. 2a) there is appreciable absorption in this region. In the case of *o*-bromotoluene in the vapour state Fig. 2(d), however, there is weak absorption even in the region 3600 Å-3400 Å and the absorption in this region is very much stronger in the spectrum due to the liquid Fig. 2(c). It is evident, therefore, that even in the vapour state the *o*-bromotoluene molecule shows much stronger absorption due to singlet→triplet transition than the benzene molecule and that such absorption increases enormously when the vapour is liquefied. Thus the substituent bromine atom in the *o*-bromotoluene molecule in the vapour state is responsible for the increase in the strength of singlet→triplet absorption and shift of the region of absorption towards red. When the vapour is liquefied the influence of intermolecular forces increases the strength of the absorption enormously in the case of *o*-bromotoluene, but only slightly in the case of benzene. If in the liquid state the dissipation of energy of the excited state by processes other than radiation would result in the shortening of the life-time of the excited state and consequent increase in the absorption such increase would be of the same order in both the liquids. The increase is, however, much larger in the case of *o*-bromotoluene than in the case of benzene. In the former case the molecule has not only a heavy atom but it also has a permanent electric moment. On comparing the luminescence exhibited by different disubstituted benzenes, it is found that the luminescence produced by chloro- and bromotoluenes is much stronger than that exhibited by dichloro- or dibromobenzenes. It appears, therefore, that not only the presence of heavy atoms but also the formation of groups of associated molecules may be partly responsible for the luminescence and absorption due to singlet→triplet transition.

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Letters to the Editor

1

ON THE VARIATION OF ELECTRONIC TRANSITION MOMENT R_e IN CN VIOLET BAND SYSTEM

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(*Received, October 8, 1960*)

Nicholls (1956) has discussed the variation of electronic transition moment, $R_e(r)$, with r for a number of band systems including the CN violet band system. He used the experimental transition probability data of Ornstein and Brinkman (1931) and obtained the following expression for the variation of $R_e(r)$,

$$R_e(r) = \text{const. } (-1 + 2.579\, r)$$

in the range $0.95 < r < 1.32\text{A}$.

Nicholls and Dixon (1958) have also studied the variation of $R_e(r)$ with r in the case of CN red system excited in active nitrogen-carbontetrachloride source and found that the expression

$$R_e(r) = \text{const. } (1 + 0.166\, r)$$

represents the variation of $R_e(r)$ with r in the range $1.04 < r < 1.27\text{A}$.

It may be noted that CN red system is due to a transition of the CN molecule from its excited $A^2\pi_i$ state to $X^2\Sigma^+$ state, while the violet system is due to one from excited $B^2\Sigma^+$ to $X^2\Sigma^+$ state. Now Bates (1949) has suggested that the variation of $R_e(r)$ with r will be larger for perpendicular ($\Delta\Lambda = \pm 1$) than for parallel ($\Delta\Lambda = 0$) band system. If Bates' suggestion contains any germ of truth, so larger a variation of $R_e(r)$ with r in CN violet system (as compared to that in CN red system) becomes doubtful.

Guided by this doubt, the recent experimental transition probability data for furnace excited CN violet system given by King and Floyd (1955) have been analysed for the trend of variation of $R_e(r)$ with r. The method used was the r-centroid method used by Nicholls in his own analysis. The variation of $R_e(r)$ with r has been found to be given in the same range of r by the expression

$$R_e(r) = \text{const}\,(1 + 0.03\,r)$$

This trend is much slower than the trend reported by Nicholls (1956) and lends a further support to Bates' suggestion.

It seems that the actual trend of variation of $R_e(r)$ with r in CN violet band system is represented by the above expression. So far as the more rapid variation of $R_e(r)$ with r obtained by Nicholls from an analysis of Ornstein and Brinkman's experimental data is concerned, it may possibly be due to some systematic error in the Ornstein and Brinkman's data.

This inference is also supported by a remark of Brinkman quoted by Smit (1946). According to Brinkman himself the accuracy of these results (i.e., of Ornstein and Brinkmans' transition probability values) has been estimated to be not high. It was always hoped that the furnace measurements will yield accurate band ratio.

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BOOK REVIEW

Proceedings OF THE INTERNATIONAL SYMPOSIUM ON TRANSPORT PROCESSES IN STATISTICAL MECHANICS, Edited by I. Prigogine, Interscience Publishers, New York, and London, 1958, pp. 436. Price $ 10.00

The present volume is a collection of 48 papers presented in the International Symposium on 'Transport Processes in Statistical Mechanics' held in Brussels in Aug. 1956. The volume has been divided into 14 parts, the theoretical papers being grouped in Parts I to XII and experimental papers in Parts XIII and XIV. The division of the book into the different parts is, however, not always quite logical.

In parts I to III the statistical mechanical basis of the steady state has been discussed from several points of view leading to the derivation of Boltzmann equation as used in the kinetic theory of gases, while part IX deals with the quantum-mechanical aspect. The other parts deal with specific problems. Transport phenomena (mainly thermal conductivity and diffusion) in solids are dealt with in Parts IV, V and VII while diffusion in gases and liquids are discussed in Parts VI and VIII respectively. Part X deals with some transport phenomena in liquids, particularly liquid helium. Part XI which covers about seventyfive pages is particularly welcome as it gives a fair idea of the controversial aspects of the basic principles of the thermodynamic theory of irreversible processes. This might stimulate activity in making the fundamentals more sound or in extending the domain of applicability of the theory of irreversible processes. In parts XIII and XIV some special experiments of topical interest are discussed such as viscosity and thermal conductivity of gases at high pressures, diffusion and thermal diffusion in gases and liquids, Soret effect, etc. The parts are followed by discussions which are quite interesting and useful.

The book gives, in a small compass, a good picture of the current effort being made to elucidate the intricate aspects of the Transport Theory from statistical mechanics. In view of the nature of the subject and the form of the book as a mere collection of papers, the present volume is likely to be useful only for research workers in the field.

<div align="right">B. N. S.</div>

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